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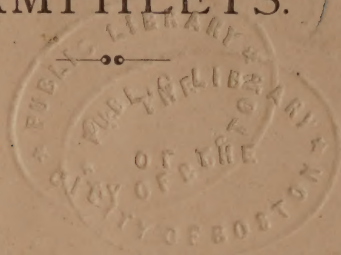
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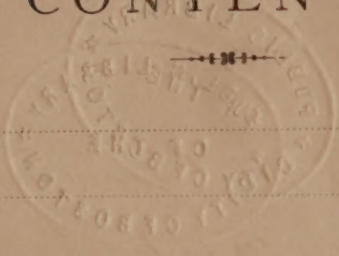
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PRINCIPLES AND OBSERVATIONS

APPLIED TO THE

MANUFACTURE AND INSPECTION

OF

POT AND PEARL ASHES.

BY DAVID TOWNSEND,

INSPECTOR of POT and PEARL ASHES for the COMMONWEALTH of
MASSACHUSETTS.

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PRINCIPLES AND OBSERVATIONS

RELATIVE TO THE ARTS

MANUFACTURE AND INSPECTION

POT AND PEARL ASHES

*THE following observations relate to an extensive business :
and are designed, in the plainest manner, to convey profitable in-
formation to those interested in it, who have not leisure or oppor-
tunity to search for the principles therein contained, in the writ-
ings of professional Chemists.*

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PRINCIPLES AND OBSERVATIONS.

POT and Pearl Ashes have for a long time been amongst the most valuable articles of manufacture and commerce in this part of our country.

To preserve and improve so great a branch of business is an object interesting and important to this Commonwealth, and, as such, has employed the attention of the Legislature. "An Act to ascertain the quality of Pot and Pearl Ashes, and for the more effectual Inspection of the same," is intended to effect this salutary purpose; and the operation of it ought to remedy evils which have deprived our citizens of the commercial advantage of their own manufacture, and our manufacturers of the highest market price for their Ashes, unless they transported them to the State of New-York for inspection. For, under our old law, the inspection was superficial. The consequence was, that the most indifferent Ashes came to our market; even the refuse from New-York was often brought to Massachusetts for exportation; while it became an object to many, who sought a market for Ashes of the first quality, to send them

from

from Massachusetts, by an expensive transportation, that their real value might be stamped upon them by the superiour credit of the New-York brand. A difference of price current obtained between New-York and Massachusetts Ashes, both in Europe and America ; and Ashes exported under the advantage of the New-York brand, would sell from three to four pounds per ton higher than that from Massachusetts.

To put a stop to this ruinous traffic, the Legislature thought proper to frame the new law, adopting a mode of inspection similar to that practised in the State of New-York, that we might participate of the benefits naturally resulting to us from this important export.

Much therefore depends on the execution of this law, and it may be of use to enquire into the principles on which the inspection and examination are conducted, that they may be fairly and generally understood.

The excellence of Pot and Pearl Ashes is in proportion to the quantity and purity of the alkaline salt they contain ; and, it appears, that in this proportion they are estimated by those who consume them.

The very best kind is sought after by chemists and druggists,—for the bleaching of fine threads, linens and cottons—and for the manufacture of the finest glass.

The dyers and calico printers require such as will not impart colour, or leave the least stain or tinge in their work.

PEARL

PEARL ASH, *First* SORT.

THIS is the alkaline salt in a *mild* state, and in a high degree of purity. It is a perfectly white substance, uniform in its texture and appearance throughout, dissolves easily in water, gives a clear and colourless fluid without sediment, except a very small portion of white earth, such as is deposited on every solution of the purest alkaline salt that can be obtained; and containing so little of neutral salts as neither to be injured by them in its use, nor depreciated in its value by their weight. Such as this is supplied in great quantities from many of our manufactories, and commands the highest price.

PEARL ASH, *Second* SORT.

SOME Pearl Ash falls short of this high degree of purity, not being properly calcined, or, as the term is, *pearled* throughout. If pearled in kettles, the finer part is an heavy meal-like substance; the lumps, hard and flinty; the whole of a yellow or greenish cast. If pearled in the oven, and not properly manufactured, it is generally very blue, not easily dissolved, and unlike that large light porous lump so much preferred in the London market. Another kind, is of a dull dead white, inclining to grey, occasioned by not settling the lye, or by dipping it so as to disturb the sediment, of which a very little will diffuse

diffuse throughout, and materially depreciate a very large quantity of Pearl Ash. All these however are valuable, being rich in the genuine salt, and are used in a variety of bleaching, and for many purposes which make them in demand; but not at the first price; therefore, they are denominated the second sort.

PEARL ASH, *Third Sort.*

WHEN the appearance of Pearl Ash is totally different from the above description, is of various colours, hard of solution, and the solution charged with colouring matter, depositing a dirty, dark sediment, it is unfit for the nicer purposes in the arts, and therefore, suffers such a reduction of price, as operates to the exceeding loss and injury of the manufacturer, if imprudently he offers it at market. Whenever Pearl Ash, under the best appearance, is found to contain a great portion of neutral salts, it is undervalued accordingly.

POT ASH.

THERE are many articles bleached, of so firm a fabric, as not to be sufficiently acted upon by the alkaline salt, in a mild state. To be thoroughly whitened, they require a greater degree of *causticity*.

The manufacture of soap also creates an immense demand for the *caustic* alkali, a quality in the alkali necessary to dissolve the oil or fat in the composition of soap, and render it miscible with water.

Our

Our *Pot Ash* is this caustic alkali. The appearance of it, very different from Pearl, soon changes from the action of the air upon its surface ; therefore, to form the first opinion of it by the eye, it is necessary to break the lumps.

P O T A S H, *First* SORT.

THE best is generally of a light stone grey, or marbled white and grey, with a crystalline core ; caustic or burning to the touch, and, although in appearance like a stone, and almost as hard, it so greedily attracts moisture from the air, that when exposed to it but for a short time the surface of this stone-like substance completely dissolves. This, which is denominated first sort of Pot Ash, is however very far from being a pure salt ; as any one may easily observe, by letting a solution of it rest, until it deposits a sediment. Yet, it is the best that is generally sent to the market, and until there is a further improvement of this manufacture, must be considered as the standard.

P O T A S H, *Second* SORT.

BESIDE the foregoing, there are large quantities of Pot Ash, of different degrees of purity, of various colours, that, on examination, merely by the eye, shew marks of heterogeneous mixture, arising from want of sufficient attention to what is called by the manufacturer, settling the lyes ;
whereby

whereby the finer earthy parts of the wood-ashes get enveloped with the salt : or, for want of proper management of the fire, not continuing it long enough, or not raising it sufficiently to destroy what the workmen call the sulphur. This sulphur which is the inflammable or black colouring matter, is most injurious to the purity of the alkaline salt, and cannot be separated from it in large manufactories, but by fire, as is hereafter explained.

This impurity, in its different degrees, is seen at once, by the different shades of red it gives the Pot Ash. In the brightest pink coloured, where it is clear, without an edging of coal black, or mixed or marbled with light grey, the black colouring matter is in so small degree that it is placed with the first sort. If it is of a deeper red, it shews a greater quantity of this colouring matter, and by wetting a piece of it, and rubbing it a little, there may be discovered a very considerable degree of foulness, that is not in the Pot Ash before described, and is therefore denominated the second sort.

P O T A S H, *Third Sort.*

WHEN Pot Ash is of so deep or dark liver coloured red as to turn black on exposing it but a short time to the air; or when wet and rubbed, it appears foul and black as the blackest ink, interspersed throughout its whole substance with small black

black specks, as if sprinkled with dust of charcoal, or imperfectly melted ; it is then almost as impure as what are called black, or Pot Ash salts.

If, as was observed of Pearl Ash, with the best appearance, Pot Ash contains neutral or foreign salts in quantity, it is depreciated accordingly.

The foregoing observations contain a very general description of the Pot and Pearl Ashes brought to the seaports of this Commonwealth, for exportation, together with an account of some of the uses to which they are applied. Further remarks may be of use to some manufacturers of Ashes, and may perhaps enable them to conduct their business with more ease, satisfaction, and certainty of success, than they have hitherto been used to ; whereby they may prevent such great loss as is sustained in transporting so heavy an article by land carriage, some hundreds of miles, as they sometimes do, in a *depreciated state*, when it has not been properly manufactured.

That there may be an understanding of the principles that should direct in this manufacture, previous to an account of the processes by which Pot and Pearl Ashes are made, it will be necessary to premise, that, although all alkaline salts obtained from vegetables when absolutely pure, are precisely the same ; yet, there is a difference between Pot and Pearl Ashes, though made from the same lye, which admirably adapts them for different uses. This difference exists in nothing

but the comparative mildness of the one, and the causticity of the other : therefore, the terms *mild* and *caustic* have been used, to express the different properties of the same alkaline salt under different forms. The mild quality depends on a principle, next to fire and water, the most active agent in this business. It has been very little attended to by manufacturers, although long known amongst chemists by the name of gaz, fixable or fixed air, and now generally denominated the aerial acid. This is absorbed from the common air, often from spring water ; and Pearl Ash in its utmost state of purity and perfection, is now known by the name of the aerated alkali.

The caustic quality of Pot Ash depends on the absence of this aerial acid, and suggests the propriety of the different modes that are practised to obtain the same alkaline salt, well prepared, for different purposes. From the beginning, through every stage of the manufacture of Pearl Ash, this aerial principle applies itself, and its operation will be particularly attended to, when we come to the pearling process.

The common hard wood throughout this country furnishes alkaline salt in great abundance : what is called soft wood, such as every species of pine, is well known to yield but little.* From
the

* S. Blodget, Esq; now living in Haverhill, formerly a scientific manufacturer of Ashes in this town, has bestowed indefatigable attention on experiments, that shew the different quantities of salts produced from different sorts of wood, growing in this country. The results
he

the manner of burning wood, either abroad in the open air, as in clearing up the land, or in chimneys, for common fuel, it is evident, that when reduced to wood ashes, the contained salt must be blended with a variety of substances, which constitute its impurity. In this state the manufacturer receives it. It is his business to free it from these foreign substances; and in proportion as he effects their separation, will be the excellence of his Pot or Pearl Ash.

Although these substances of impurity are almost infinite, yet they may be classed under three heads; 1st. Some earthy substances insoluble in water. 2d. Colouring matter. 3d. Neutral salts.†

As the difference between Pot and Pearl Ashes has been stated to be but a different manufacture of the same salt; whereby it acquires the different properties already noticed, the two processes for their manufacture must be treated of separately; therefore, the first observations will be confined to the process for the manufacture of Pearl Ash.

Experienced

he has been careful to preserve, as useful knowledge, which, together with other facts his accurate observation has furnished, or his experience confirmed, it is hoped he will be induced to communicate.

† Another source of impurity not mentioned above, though it might be comprehended under the article, colouring matter, is from iron; this united with alkaline salt, fixes so strong a dye, that the best mode hitherto practised for its separation will not indemnify the manufacturer of Pot Ash, for the trouble and expense of it. Therefore, although even this may be separated with great care and trouble, it will be most for his interest, whenever the water to be made use of in leeching is found to be from a spring impregnated with iron, to seek for a new supply where it may be had more pure, or give up the attempt to make good Ashes.

Experienced manufacturers find an essential difference in working wood ashes that have been collected from abroad, or, that have been long exposed to the air ; and those that are recently made under furnaces, or even in common chimneys. They remark, that salts from wood burned abroad, when clearing up the land, will not easily melt, but will pearl without difficulty, and are often determined in their arrangement for making Pearl or Pot Ash, from this circumstance. Many conjecture the cause of this difference to arise from the common earth or dirt which unavoidably mingles with wood ashes when collected from the ground. But as leeching them and settling the lye, so as completely to separate all that is earth from the salts, does not dispose them to melt, this opinion appears without foundation.

The true cause is the principle already hinted at. It is the combination of the aerial acid, which is made evident by a variety of experiments, shewing, that wood ashes, when exposed to the air of the atmosphere, freely imbibe this principle from it, and that depriving them of this principle, is sufficient to render the alkaline salt from them caustic, and disposes it to melt.

—•••••

The PROCESS for the MANUFACTURE of PEARL ASH is carried on by several operations :

LEECHING.

LEECHING.

THE first consists in dissolving and washing out all the salts from the indissoluble earth or dirt, with pure rain or river water, if to be procured; in filtering, or straining it nicely, and in letting all sediment subside, or settling the lye. This is called leeching the wood ashes.* It is so well understood and practised by many of our manufacturers, that it would be unnecessary to be minute, did not too many adhere to the old mode of sinking huge leeching vats under ground. Defects in them are thereby so concealed, that a great loss of lye may be sustained before the workman discovers the leak. The heavy compact mass they contain, is not so easily soaked and washed as a smaller body: not readily admitting the water throughout its whole substance, passages are sometimes formed by gutters through various

* It has been strongly recommended to begin this manufacture by calcination, or burning the wood ashes in an oven or furnace. But the experiments hitherto made, have only served to prove this an expensive and troublesome mode, without the advantage boasted of and promised by Mr. S. Hopkins, the author of this supposed improvement.

Water is the proper solvent of all salts, and where the combustion and incineration of wood ashes has been complete, it is a fact not to be controverted, that boiling water will thoroughly dissolve and wash out all the salts, of every kind, blended with the earth in wood ashes. If the wood has not been completely reduced to ashes, but to ashes mixed with coals, then would it not be better, by sifting them, to separate the coals, which, thrown under the furnace for fuel, would be calcined with profit? Another advantage to be derived from this mode would be, lessening the quantity of colouring matter that is imparted by coals, &c. therefore would facilitate an after part of the process.

various parts of the vat, where any quantity of water will run without penetrating beyond the neighbourhood of the channels it has made ; and although the water passes through the ashes until it becomes tasteless, and receives no augmentation of weight (which is the criterion to determine when wood ashes are leached) yet much of the contents of such a vat may be strongly impregnated with salts.*

A more important objection is, that the lye after it is strained and settled cannot be brought to the kettle in that state of purity that is necessary, unless it is settled again; for it must be drawn up from the cistern by the suction of a small pump, or dipped out with a bucket or ladle, either of which, however carefully performed, disturbs the sediment, that is always deposited, although the lye has been well filtered, and renders it foul, beside occasioning an increase of labour.

Leeching

* It is not improbable that some partial experiments with wood ashes, thus imperfectly leached, may have given rise to the opinion that dead ashes (i. e. such as already have been leached) might, under the operation of the supposed improved mode of burning ashes, afford a sufficient quantity of alkaline salt, for another manufacture of Pearl Ash.

However the opinion of this extraordinary creation of alkaline salt prevailed ; its effect was, that although the rational foundation of hope and expectation, (i. e. that the principle on which the new product was to be obtained) was concealed in profound mystery, hereafter to be revealed ; the idea was so captivating as to engage numbers in a new project, who destroyed their well constructed furnaces, to erect such as on experiment became useless, and entered into incredible contracts for leached ashes, that would not pay for their transportation. Within the term of two years, this business terminated in disappointment, to the loss and mortification of all who pursued it.

Leeching is better performed in vats placed above ground, where they are always under the eye and examination of the workman. In small vats, the wood ashes can be more easily and thoroughly drenched than in large ones; instead of vats that will contain 80 or 100 bushels, those that do not exceed 30 are to be preferred.

Each vat is to be provided with a false bottom, so tightly placed above the true one, as to admit nothing below but what is dissolved and carried down by the water; for this purpose, there should be a number of small holes, cracks or channels, in the false bottom, covered over with straw, to prevent the passage of the earth while it admits the lye.

The distance of the false bottom from the true one (which forms a receiver for the lye, and is called the cistern of the vat) should not be less than six or eight inches, that the sediment which falls, may rest at the bottom of the cistern; while the lye is drawing off from a faucet placed at a convenient distance above it. The upper part or body of this vat is to be filled with the wood ashes, within two or three inches of the top, and as much water is to be poured on them as they will absorb, and will cover them to the brim of the vessel. This done over night, the lye may be run off in the morning.

The number of vats should be in proportion to the extent of the manufactory, and the number of kettles employed, so that there may be a constant

constant supply of strong lye, for boiling down. This part of the business should be managed after the manner practised in distilleries, to have a succession of a certain number of vats ready to work off, and furnish every day's boiling : and where it is practicable, they should be so arranged that the lye may be conveyed from one vat to the other, and from them into the kettles by a spout.

Whenever the lye toward the close of leeching becomes so weak as not to pay the expense of time and fuel to boil it down, it should be thrown on to another vat until it becomes tasteless, and receives no augmentation of weight by the leeching. The vat is then to be emptied, the false bottom taken out, the whole examined and cleansed for use again.

The foregoing operation gives a solution of all the salts of every description that were contained in the wood ashes, effectually separated from the earthy impurities, but yet combined with the colouring matter. This solution is next to be boiled down to the consistence of brown sugar, to prepare the salts for the first calcination or scorching, which is the second operation, designed to separate and destroy the colouring matter, and convert black salts into white. This colouring matter, known to workmen by the name of sulphur, sometimes improperly called the *caustic sulphur*, or *oil*, has been denominated, by the most celebrated chemists, the inflammable principle, and

and is, according to one of them, “ the material which, with iron, forms Prussian blue in alkaline salts, occasions their impurity, and requires much trouble to be perfectly separated.”† In fact, as has been said, it cannot be separated in large manufactories, but by fire.

SCORCHING.

FOR this purpose, when the salts are of the above consistence, they are to be thrown into a furnace so constructed, as to admit the utmost force of flame immediately upon the salts, while they are exposed to a continued current of air.

The furnaces in common use for scorching and pearling, are well constructed; they completely reverberate the flame on the salts, at the same time that they admit a continued stream of air necessary in this operation, which is a genuine calcination, and cannot otherwise be performed. In this situation the salts are to be frequently stirred, that every part of them may present its surface to the two powerful agents. A strong fire may be applied, but not so intense as to melt them. When the salts have this tendency, the greatest care must be taken to avoid it, by moderating the fire, and by keeping the door of the furnace open, to expose them still more to the air; for if they

begin

† Chemical Dictionary, Article Prussian Blue.

begin to run, it is difficult to proceed with the operation, which, if imperfectly performed, must disappoint the hope of the manufacturer for a successful termination of the pearling process.

This first calcination is known to be finished, if the salts, when wet or dissolved, have lost the strong disagreeable smell of black lye, as well as the colour, which is now changed for white.

TO SEPARATE NEUTRAL SALTS.

THE next operation is, to wash away the colouring matter that has been separated, though not completely destroyed by scorching, and to separate the neutral salts.

These objects are very conveniently effected at one and the same time, simply by solution, in such a quantity of boiling water as will take up the alkaline salts, but when cold will not hold the neutral salts in solution. This point is attained sufficiently accurate for this manufacture, and depends on the different degrees of solubility of different salts.*

When

* Several kinds of neutral salts are found with the alkaline salt leached from wood ashes; they vary in their quantity and proportion from a variety of circumstances, according to the kind of wood they are made from, and the state of it when burned. From old dry perishing wood, the neutral salts are in great abundance: If the wood has long been soaking in sea water, uncommon quantities of marine, or sea salt, will be found. Water from wells and springs dissolves different salts it meets with in its passage through the earth, and when made use of instead of rain or river water, it increases the neutral salts,

When salts produced from good sound wood are fairly made, without any designed adulteration, a solution of them that will weigh a very little more than one quarter heavier than the same measure of pure rain water, when drawn into a receiver, where it must be at rest until cold, will deposit the neutral salts in crystals round it; and while this is taking place, if the salts have been well scorched, the remaining colouring matter, and all sediment, will be found to have subsided at the bottom of the receiver.

Here it cannot be too strongly impressed on the workman to avoid every thing that will in the least degree disturb the sediment. It is an object so important to be attended to, that it cannot be amiss to repeat the injunction on this head, that he ought never to take this lye from the receiver by pumping or dipping. He will ever be apt to dip too near, and the smallest quantity

salts, and sometimes diminishes not only the proportion, but the absolute quantity of alkaline salts already obtained in the wood ashes. Those acquainted with the nature of salts readily perceive how this must happen, when a neutral salt, with an earthy basis, is dissolved in an alkaline lye. The earthy part of the neutral salt is dropped and exchanged for a portion of the alkaline salt taken up to form a new neutral salt.

This lessens the quantity of alkaline salt by as much as is taken up to form the new combination, and in exchange for it is added the earthy impurity, while, although the kind of neutral salt is different, the quantity remains the same. On a fair calculation, this will be found to cause no trivial deduction from the real quantity of alkali which might be obtained from the same wood ashes if pure rain water was used. On an average five hundred bushels of wood ashes are drenched and leached for a single ton of Pot or Pearl Ash.

quantity of sediment raised, will diffuse through the whole such a dull white appearance, more or less inclining to grey, as induces a suspicion in the purchasers of Pearl Ash, particularly on the other side of the water, of a mixture of lime; which suspicion has depreciated great quantities of ashes otherwise good.

This is easily avoided, by drawing off the white lye from a faucet placed above the sediment, as described under the head of leeching.

It cannot be objected to the above mode of separating the neutral salts, that some small portions of the alkaline salt will be thrown down with them; because, washing the crystals of neutral salts in cold water, not sufficient in quantity to dissolve them, will dissolve the remaining alkaline salt, which, with the sediment, may be thrown on to one of the vats for a new process. By the above mode may be drawn off into the kettles, nicely cleaned to receive it, a pure white lye, to be boiled again down to salts for the finishing operation, which is the second calcination, called pearling.

PEARLING.

IF scorching has been well performed, the pearling operation is made easy; being little more than drying the white salts in the pearling oven or furnace, with a moderate clear flame. It is

an operation similar to scorching, but does not require the same force of fire; the salts having been previously freed from their impurity. When boiled to the consistence of salts, they are to be thrown into the pearling furnace, and continued under this last operation in the manner they were scorched, until they are perfectly whitened, and found to be of the description of the first sort of Pearl Ash.

It is to be again noticed, that as some salts are found more tender than others (i. e.) more disposed to melt, they require more particular care and attention to moderate the fire and increase their exposure to the air.

There is another mode of pearling much practised of late, which will be found exceptionable, whenever the requisites for this operation are taken into consideration. It has already been observed that pearling is a genuine calcination; and, that a continued stream of air is so necessary in the operation, that it cannot otherwise be performed. It is evident that this cannot well be had in the bottom of a deep kettle; for, when heated, the air is expelled from it. A broad or shallow pan would answer better; but no contrivance can exceed the furnace that will throw a clear flame directly upon the salts.

Beside that it is impracticable to expose the salts to such currents of fresh air in the kettle as in the furnace; it is obvious, that when the fire under the kettles is likely to be raised too high,

high, by the time the operator is apprized of it, it is often too late to prevent the mischief it must occasion, on account of the continuing heat of the iron. Therefore, the salts, for want of sufficient exposure to the air, and by reason of too great heat, have not imbibed their portion of the aerial acid, and are thereby rendered caustic, and more disposed to melt.

Hence the reason, that, although two or three manufacturers, by extraordinary care and caution, have produced Pearl Ashes of the first sort in this mode; yet, in this way, great quantities have been sent to market imperfectly pearled; much of it fine, not well dried, heavy, and like meal of a yellow tinge; while the lumps beginning to melt, are externally hardened, and of the same or a greenish hue.

The causticity of this kind of ashes gives it an appearance of greater strength. But this property cannot be a recommendation of it, while those who use it for nicer purposes, where the *mild* alkali, or first sort of Pearl Ash, is required, find it too corrosive, or sharp, for their work.

This kind of kettled ashes is in disrepute in the London market; and on account of its corrosive quality, is sometimes suspected of being heated with lime. This suspicion, however, must be groundless; for, did the manufacturer attempt to use quicklime in *kettling* ashes, it would inevitably melt the salt.

To

To finish the observations on the manufacture of Pearl Ash little remains to be said, except what relates to putting it up or packing it for the market. Neatness in this part of the business quickens the sale, and often enhances the price of the article, above the difference made in its intrinsic value. The eye of the purchaser, particularly in the London market, is prejudiced, beyond what is commonly imagined, even against good ashes when not shewn to the best advantage.*

If Pearl Ash is tight packed, the lumps are broken, and it is made fine : It is true the property of it is in no degree altered ; it is equally as good for every possible use as though it were in large lumps, smoothed by rolling loosely in the cask ; yet it does not meet with the same approbation, and has been frequently complained of.

A want of neatness, which proves an essential injury to Pearl Ash, is frequently occasioned by a mixture of scorched salts : it is impracticable to separate them when repacking, especially if the Pearl Ash has been pounded almost to powder, to crowd the greatest possible quantity into a cask. This impurity is too often in such proportion as to denominate the Pearl Ash second fort.

* A letter lately received from a house in London that perhaps deals as largely in ashes as any one house in Europe, contains the following observation. " Small ashes, however pure, will not recommend themselves in England like bold ashes of a good colour."

fort. To prevent it altogether, it is found most convenient and best to use separate furnaces ; one for scorching, another for pearling. Where the business is not sufficiently extensive to afford the expense of two, the single furnace, after it has been used for scorching, should be most attentively examined, and thoroughly cleansed of all remains of scorched salts. The hearth also should be noticed, and repaired if necessary, that there may be no pieces crumbled from the bricks of the furnace found amongst the Pearl Ash.*

By

* Sometime in the course of the last season, amongst six or seven casks of Pearl Ash sent to the Inspection Store, one of them was marked second fort ; because, with the Pearl Ash, there were small pieces of brick and mortar that had crumbled from the inside of the furnace, interspersed throughout the cask. The person who brought it, alledged that the Pearl Ash being very good, so trifling and accidental a mixture could not materially injure it for use ; therefore the second fort brand would depreciate the value of the Pearl Ash, and not the few foreign substances found with it. The owner and the Inspector, as is very common, differed in opinion, and the Pearl Ash passed as second fort.

A workman from the glass house came to the store, examined for himself, and liked the appearance of this Pearl Ash, and it was purchased for that manufactory.

When the melted composition, wherein this was an ingredient, was to be blown into plates of glass, it was snapped in pieces by the brick, before the plates could be formed. By which mischief the blast was lost, and the proprietors, from this single cask of Pearl Ash, in one evening sustained an injury to the amount of between 30 and 40 dollars.

BY a different process the same alkaline salt is obtained in a caustic state, and is called

P O T A S H.

IF the essential difference between Pearl and Pot Ashes is the comparative *mildness* of the one, and the *causticity* of the other ; and if the mildness of the alkali in Pearl Ash depends on its combination with the *aerial acid* (a principle it absorbs from the common air, or from *hard* water used in the manufacture of Pearl Ash) we are at once presented with a key to that mystery whereby good Pot Ash can *always* be made.

Prevent as much as possible the combination of this aerial principle with the alkaline salt, while passing through the different operations, to free it from its impurities : deprive it of what it unavoidably catches, and the process must be successful.

To prevent then this combination, the wood ashes, or the salts from them, should not be exposed to the open air ; for although the free admission of air is requisite in calcination, as has been insisted on throughout the pearling process ; the exclusion of it in fusion, facilitates that operation ; and *melting down*, as it is termed, is well known invariably to succeed better the less the external air is admitted. The only reason why alkaline salts should be melted into Pot Ash, is, that by the force of so strong a fire,

the aerial acid may be expelled, that the alkaline salt may present as small a surface to the air as possible, and thereby retain its remarkable causticity.

This remarkable property is greatly increased by the use of quicklime, which property also increases the fusibility of the alkaline salt, or its disposition to melt; therefore to deprive the alkaline salts of the aerial acid which they had imbibed from the air, or from the hard water used to dissolve them, quicklime may be used, not only without injury to the Pot Ash, but with advantage.

There is no substance in nature known to possess so great a share of the aerial acid in its composition as that which makes the best of quicklime. This aerial principle being expelled from *limestone* by fire, in the manufacture of quicklime, it becomes a *caustic* substance, ever ready to regain its natural state; and it will most greedily absorb what it has been so violently deprived of, whenever circumstances favour it.

Present alkaline salts in a *mild* state to quicklime, and in proportion as they possess this aerial principle, it will be restored to the quicklime, which will thereby become mild, or slacked, leaving the alkaline salts possessed of their original caustic property.

The foregoing principle admitted, directs to the proper use of lime, and shews that after it has
thus

thus acted on the alkaline salts, it serves only as a strainer, and therefore the lye ought to be as carefully drawn from it, as from any other earthy impurity. It also shews the advantage that will result by excluding the air as far as practicable, from the wood ashes designed for this manufacture, from the lye, and the salts, through every operation of the following

PROCESS, for the MANUFACTURE of POT ASH.

THE first operation consists in *leeching*, as for Pearl Ash.

This has been so particularly treated of, that a repetition would be useless, although the most minute attention to every circumstance there noticed, is indispensable. A difference too, to be observed, is, that here unslacked lime may be used. The straw upon the false bottom of the vat is to be covered first with wood ashes, then as much unslacked lime is to be thrown over it, as, when slacked, will make a layer of three or four inches; that the lye passing through may not only be strained, but that it may acquire a more caustic quality. An additional quantity of lime may sometimes be requisite to be thrown into any part of the vat with the wood ashes, when they have been rendered more mild than usual, by long exposure to the air.

When

When the lye is leached and settled, it is to be drawn off into the kettles, and boiled down, for

THE SEPARATION OF NEUTRAL SALTS.

THE boiling is to be continued until a scum is observed to collect on the surface of the lye, or, until it will weigh a little more than one quarter heavier than pure rain water. It is then to be taken from the kettles into a receiver, where it is to be again settled by throwing into it another quantity of lime, unslacked,* to increase its causticity. The

* Here an enquiry presents itself that may be thought to deserve more particular discussion. How much quicklime is to be used in a given quantity of lye? No explicit answer can be given to this question. No definite quantity can be determined on for different parcels of lye, which already, without the addition of lime, possess different degrees of causticity. (e. g.) From wood ashes recently burned, immediately taken from under a furnace before they are cold, and carefully leached with pure rain or river water; or, if early in the season, even with good spring water, no quicklime will be requisite. The salts have not been exposed to absorb the aerial acid, they will therefore be sufficiently caustic, and will melt like oil. Take wood ashes of the same description, that have been exposed to the air for months together, let them be leached in the common mode, with water from the same spring in autumn, when it runs low and becomes hard; the salts will have absorbed so much of the aerial principle from the air, and from the water; that unless quicklime be used to absorb it from the lye again, they will prove extremely hard to melt.

A simple experiment will shew the difference between the two lyes, and tends to establish the principle, that the state of the last lye depends on the aerial acid. To a glass of it, pour by degrees a little sharp vinegar or other acid, and it will immediately be thrown into a violent state of effervescence, caused by the sudden expulsion of air the alkali has absorbed, which must give place to the new union with a stronger acid. But if the alkali is completely caustic, no such effervescence.

The receiver is to be covered, where the lye should rest until it is cold, when it is to be drawn off as carefully from a faucet placed above the sediment, as directed for the white lye, designed for Pearl Ash. In this way the neutral salts and all sediment will be left in the receiver, and the lye prepared for the last boiling. For this, the utensils, the kettles, and every thing about them, should be very clean, that no impurity fall into the lye. After it is drawn off and conveyed again into the kettles, they should be covered until the lye begins to boil, that it may not lose of its causticity. The covers may then be taken off, to favour its evaporation. When dried down to salts, the fire is gradually to be raised; the kettles again covered for

MELTING.

IF the precautions recommended have been duly attended to, this operation, often tedious and expensive, hazarding the loss of kettles, and perplexing the workmen, becomes at all times easy and expeditious, and *melting down* terminates the process to the complete satisfaction of the operator. For by the time the alkaline salt is well melted, the last impurity, the black colouring matter is destroyed; but, if the alkaline salt

effervescence is seen immediately on the mixture of an acid; there is no air to be expelled, and the union of the acid with the alkali quietly takes place.

When then a violent effervescence suddenly commences on the mixture of an acid with the alkali, quicklime may be added to the lye with advantage.

salt is not caustic, by being kept or freed from the aerial acid, and the neutral salts have not been separated; it is extremely hard to melt. And the black colouring matter* is so strongly united to it, that if after a tedious length of time with excessive fire, it is melted without breaking the kettles, the Pot Ash will be found red and foul, although the lye has been leached and settled in the most careful manner.

Dr. Lewis, one of the most eminent of modern chemists, in his valuable little treatise on Pot Ash, observes, when treating of the mixture of sea salt with American ashes, that "as almost all the common sorts of sea salt participate of the bitterness of sea water, the combination of the vitriolic acid of that salt with the inflammable matter during fusion is probably the origin of the sulphureous taint;" (*i. e.* the black colouring matter) "in Pot Ash." If this is true, we are taught to explain the effect that all other neutral salts, as well as sea salt, have on Pot

* This colouring matter has been improperly called the *caustic* sulphur, and the *caustic* oil, from a conjecture that it was the cause of *causticity*. This error probably was suggested by observing that black salts oftentimes retained a considerable degree of caustic sharpness, which they lose at the same time the colouring matter was destroyed by calcination. However respectable the authorities are that formerly held this opinion, it is now a fact well established, that the *causticity* of the alkaline salt does not reside in the inflammable principle (*i. e.* in the black colouring matter) but that it is really diminished in proportion as the inflammable principle abounds.

Neither has this colouring matter the properties of an oil—if it had, it would invariably form soap by its union with the alkali.

Pot Ash; for all other neutral salts found with the alkaline in wood ashes, are combinations of the vitriolic acid with different bases; therefore, the same effect is to be expected from the vitriolic acid in their combination, as from the same acid combined in the bittern of sea water. Again, if hard water has been made use of instead of soft, it has a similar effect on the Pot Ash; the salts are very hard to melt, and the black colouring matter remains; and it becomes almost impossible by the common mode of manufacturing to destroy it.

Water is made hard, not only by neutral salts, but by the aerial acid.*

Well and spring water, although at sometimes sufficiently soft and pure, when the springs are low, become hard by this impregnation.

Here is disclosed the mysterious cause of Pot Ash salts melting easier in the spring and the fore part of summer, when the whole earth is filled with water, than at the close of the season, when it is much exhausted, and the springs run low. At this latter season most spring water is hard, and it is generally said to be impossible to make good Pot Ash. Although rain or river water is always to be preferred where it can be had, especially at the season when it is thought impracticable to make good Pot Ash: Yet, indisputable experiments have proved, and must convince all who make

* The gaz which waters frequently contain, is another cause of the hardness of water. Chemic. Dictionary. Note to the article water.

make them fairly, that, according to the foregoing theory, even lye made with spring water may be so deprived of neutral salts and the aerial acid, as that Pot Ash of a *superior quality* may easily be made at *any* and *every* season of the year.

If this is well understood, the workman will no longer be astonished that his Pot Ash has sometimes proved bad; although, as he supposed, he had used the same method to cleanse it, (i. e. he had leached, settled, and drawn the lye from all earthy impurity in the same manner) as when it turned out good. He will hereafter regard the neutral salts as an impurity, and attend particularly to their separation, while through the whole process he strives to prevent the union of the aerial acid with the alkaline salts, or carefully deprives them of it when unavoidably combined. This done, melting down will soon be effected, by gradually raising the fire until a red heat is produced. Except when there is occasion to examine the melting mass, or to stir it together with a ladle, it should be kept covered, increasing the fire until it becomes an uniform thin fluid.

Iron kettles for coolers are now to be made ready, by heating them at the mouth of the furnace. A little tallow may be lightly rubbed over the inside surface of them, to prevent too strong an adhesion of the Pot Ash to the iron, which sometimes happens and is troublesome. The furnace is to be well tended with a continual supply of dry fuel to keep up a very brisk fire, to-
ward

ward the close of the process. In this state, the melted salt need be continued but for a short time to destroy the inflammable principle, or black colouring matter; the destruction of which may be known by the easy experiment of making a very strong solution of the Pot Ash in a cup of water, immersing therein a piece of silver or bright tin; if by this, the metal is not tarnished, the process is finished; and the Pot Ash is immediately to be dipped off into the coolers, taking especial care not to suffer the least abatement of fire until the kettles are emptied.

When the Pot Ash becomes hard in the coolers, and cool enough not to endanger burning the cask, before it has attracted moisture from the air, it should be packed in dry, tight, new casks, that the air may not form a crust upon its surface.

One general observation, applicable to most kinds of business, is peculiarly adapted to both the preceding processes, viz. that every operation well conducted, makes easy and shortens those that come after, and is of so much consequence to the succeeding ones, that it is best to repeat it, whenever any one is interrupted.

Such management of the business, will, at once, put an end to all well grounded complaints, against ashes, exported from Massachusetts. Instead of *second* and *third sort*, which are a dead loss to the manufacturing interest, there need not be a single cask but of an excellent quality. We shall no longer hear of "mixed parcels of ash-

es," so various in their appearance, as to beget unfavourable suspicions of their being the genuine salt. And a faithful comparison with the exports of our sister State, New York, formerly our rival in this important branch of commerce, will cease to be to our disadvantage. And while there is a market for ashes, those exported from Massachusetts will meet with a quick sale, and at the highest price. Added to this, which is perhaps the strongest and most persuasive argument for the mode of manufacturing on the principles here advanced ; experience will prove it less troublesome, more expeditious, and less expensive, than to manufacture such ashes as turn out of inferior quality, and are denominated second and third sorts.

EXPERIMENTAL

EXPERIMENTAL ASSAY OF ASHES.

THE several operations to free ashes from impurity, point to “ the more effectual inspection of the same ;” whereby the quality of any parcel may be more fully ascertained.

A solution of Ashes in rain water will determine what proportion of sediment, or indissoluble foul earth, is enveloped with the salt. By filtering it through loose wrapping paper, what remains on the filtering paper may be accurately weighed ; it will also shew the black colouring matter of red Pot Ash floating in the solution, like a mixture of lampblack. The weight of this impurity being comparatively nothing, the degree of foulness is judged of by the deepness of the dye.

Except sea salt, the neutral salts are easily discovered by the ready method practised by Mr. Blodget : It is to dissolve as much ashes as can be taken up in a tumbler of boiling rain water, and to cool it suddenly by immersing the tumbler into cold water. The neutral salts will hastily shoot, and form an apparent congelation. Sea salt, not being obedient to the same law, but being equally soluble in cold as in hot water, is not discovered by this mode ; but by slow evaporation.

Sea, or common salt, is seldom found in quantity, either in Pot or Pearl Ash, unless added by design. A pretext is sometimes made use of, that it facilitates the melting of Pot Ash. Some have
been

been induced to believe this, but they have deceived themselves ; and where melting is the only aim, a single fair experiment will determine them to give up the practice, in favour of the prudent use of quicklime, previous to the melting stage of the business.

If Pot or Pearl Ash is overcharged with neutral salts, it is suspected by the touch and taste. If instead of the *caustic* alkaline salt, any other salt be mixed in Pot Ash, it will not give that acute sensation of heat, on handling, or to the taste, as the genuine salt never fails to excite ; for all neutral salts, except the *metallic*, excite rather the sensation of cold than of burning heat. The adulteration with common salt has this effect on the Pot Ash in a remarkable degree. A solution of Pot or Pearl Ash, containing common salt, may also be discovered by its taste, if compared with a solution of ashes known to be free from it : And if these solutions are made in six or eight times their quantity of pure rain water the difference will be very distinguishable. The degree of adulteration may be found by evaporating a solution of ashes very gradually, until the neutral, and of course the common salt, will crystalize, while the alkaline, is held in solution.

But, as the quantity of alkaline salt is the object of the essay, and not what are the different kinds of neutral salts blended with it, in Pot or Pearl Ash ; the peculiar properties of that salt furnish another mode of examination that cannot deceive.

Alkaline

Alkaline salt is well known to possess the strongest disposition to unite with acids, to a certain point called *saturation*; which totally destroys the properties of both, constituting a neutral salt: until sufficient acid is added to the alkaline salt to bring it to this point, the alkali predominates, and the mixture retains its alkaline character; beyond it, the acid prevails.

A clean solution of Pot or Pearl Ash, freed from all sediment, contains nothing but salt. The question is, what portion of the contained salt is alkaline? Add an acid until the solution is neutralized, and mark the quantity of acid consumed. If neutral salts have been already blended in the solution to be assayed, it is plain it will not take up as much acid to saturate it as an equal weight of a solution where no neutral salts are blended. Those ashes therefore which will take up the greatest quantity of acid to saturate them, contain most alkaline salt.

The point of saturation is pretty well known by the taste, to those accustomed to compound acids with alkalies. The sour sharpness of the one, and the corrosive heat of the other, are not to be distinguished in the saturated mixture, because they have destroyed each other. A cessation of the effervescence that takes place on the union of an acid with a *mild* alkali, is the usual method to determine this point. But, if the alkali is completely *caustic* no effervescence takes place, for want of the *aerial acid*, that discharged by the union

union of the *mild* alkali with a stronger acid, occasions its effervescence.

The distinct properties of acids and alkalies in their action on the blue juices of vegetables, have enabled chemists to come at this point of saturation with the greatest exactness.

Alkaline solutions will invariably change the blue of vegetables to green. Acids will change the same blue to red,* while the neutral salt resulting from a saturation of the two, produces no alteration of colour.

Tinge a solution of alkaline salt, green, with some vegetable blue, add an acid until the blue colour is recovered, and the point of saturation is gained. If more acid is added the solution will redden.

The infinite variety of blue flowers, in the season of them, will supply the blue colouring matter

* Professor Bergman says, "The general rule, namely that blue vegetable juices are made red by acids, and green by alkalies, is liable to two exceptions, already known, viz. lackmus is rendered more intensely blue by alkalies, and indigo dissolves in vitriolic acid without any change of colour." Vol. II. page 129.

What is said of lackmus and indigo is undoubtedly true ; still it does not furnish any exception to the general rule, when it is remembered that neither of those substances is of the blue vegetable juice in its original state. Lackmus is a preparation of the vegetable called Archil, which vegetable, in its natural state, gives out a red colour ; but when bruised, and the red juice treated in a certain way with lime and volatile alkali, and evaporated to a consistence, it is changed into a blue pigment called Lackmus.

Indigo is well known to be obtained from a vegetable, by fermentation ; and fermentation totally changes the property of every vegetable and animal substance.

ter for this test. But they are not always to be had fresh; lackmus, a preparation of archil, is recommended because it is not so perishable.—In want of these, during the winter season, I accidentally made use of the red cabbage; a strong infusion of it in rain water gives a good blue; and I since find this vegetable recommended in preference to all others, for the trial of alkalies and acids.

It is simply prepared by pouring boiling water upon the red cabbage leaves, cut small, and let stand until cold, when it may be poured off for use.

Any acid may be made use of, even vinegar. The marine acid, called spirit of sea salt, as sold in the apothecarys' shops, will be found preferable to any other, for the purpose.

Add to one part of spirit of sea salt, ten parts of rain water, and the acid will be reduced to a suitable strength for the trial.

To ascertain with the utmost precision the *absolute* quantity of what is purely alkaline in any solution of salts, requires so minute an attention to every variation of temperature from hot to cold; to the different degrees of pressure of the atmosphere, in damp or dry weather, and to the precise strength of the acid made use of, as cannot be had without the assistance of expensive instruments; and would prove much too tedious and troublesome for common business.

Chemical

Chemical and philosophical researches require this accuracy in experiments, lest erroneous deductions should be made from their results. But it is by no means necessary to be thus scrupulously exact to determine the purity and consequent comparative commercial value of Pot and Pearl Ashes. This may be done with great ease and certainty, and with little apparatus. The apparatus need consist only of a little vegetable blue, and some acid prepared as above—two or three glass tumblers, a vial that will contain four ounces of rain water, and a small pair of scales and weights; the weights to conform to the vial and contained water: *e. g.* one weight that will exactly balance or tare the empty vial—one that will weigh precisely as much as the quantity of rain water the vial will contain, *i. e.* four ounces.

The four ounce weight may be marked 128

One two ounce, do. do. 64

One ounce, do. do. 32

One half ounce, do. do. 16

One quarter ounce, do. do. 8

One eighth, do. do. 4

One sixteenth of an ounce, do. do. 2

One thirty-second, do. do. 1

By thus marking them they may be denominated carat weights.

Take then one ounce, or thirty-two carats of such Pot or Pearl Ash, as having been faithfully made from good wood ashes, is known to be of the best quality. Let it be pulverized, that

solution

solution may be more speedily made) make the solution of it in a tumbler, in four ounces of pure rain water.

Take also an ounce of the Pot or Pearl Ash to be examined, make a like solution of it in a second tumbler in the same quantity of rain water. When the solutions are complete, and the sediment of each has subsided, pour carefully from the first tumbler half an ounce, or sixteen carats by weight, of the clear solution; add to it one tea spoonful of the vegetable blue infusion—take by weight of the prepared acid—add of it gradually to the solution that has in it the vegetable blue, and it will be found gradually to change colour, until, by repeated addition, the blue colour is restored, which shews the point of saturation. The last additions should be made with great caution, or too much acid will suddenly change the colour of the solution to a deep red. To carry this test to a point instantly discernable, I have generally added the acid until it gave the solution the first tinge or blush of red, which although a degree beyond saturation, is as precise a point, and easily determined. After this, the remaining acid is to be carefully weighed, and the quantity consumed in the trial to be noted.

Proceed immediately to the examination of the solution in the second tumbler. Take the same quantity, i. e. half an ounce by weight. Use the same test, and when, by the same caution, under

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similar

similar circumstances, the solution is brought, by the acid, to the very first blush of red, weigh the remaining acid, which will shew the exact quantity consumed.

If then the sixteen carats weight of the solution of the first tumbler, which may be called of the standard ashes, has taken up forty carats weight of prepared acid; and the same weight of the solution of the second tumbler, has taken but thirty-six carats to bring it to the same point, it is plain, that although the quantity of salt contained in each be the same, yet, of the salt that is valuable, i. e. the alkaline salt, there is a difference between them of ten per cent. The remaining salt of the second ashes being of a different kind, shews the existence or mixture of some neutral salt that ought never to have been blended, or should have been carefully separated in the manufacture.

Every expence on such ashes (the original price of the stock only excepted) being the same with the first, the profit of it must be much reduced.

In this way may be determined the comparative worth not only of Pot and Pearl Ashes, but of all Pot Ash Salts; and the manufacturer need no longer be subject to imposition in the purchase of them. A very little practice will familiarize and make easy the trial, and it will be found sufficiently expeditious. Those who collect ashes at the stores in various parts of the country, may have it in their power

to

to ascertain the quality of their purchases : and the exporters, if they please, may determine, as well as the Inspector, what ashes will be most profitable to the consumer. The manufacturer likewise may always know how his ashes ought to be received at market ; and blind indeed must he be to his pecuniary concerns, if ever he suffers ashes of the *third sort* to be sent from his works. Let him rather, if by accident he is unfortunate in a process, and his ashes prove third sort, keep the advantage of working them over to himself : This will at all times afford him greater profit than to dispose of them in any other way.

Well persuaded that nothing is wanting but the practice, to convince of this fact ; may we not expect the time, which probably is not far distant, when what are now denominated *third sort* of ashes, may not be known or heard of in the Massachusetts market ?

APPENDIX.

A P P E N D I X.

PEARL ASH FURNACE.

IT is not easy to give an accurate description of a Furnace, unless by reference to a plate where it is delineated. A general idea, however, of the Furnaces employed in the business treated of, may not be altogether useless.

A Furnace, whether for scorching or pearling, should be exactly of the same construction: It is properly called a *reverberatory Furnace*, and differs very little from the *reverberatory Furnace* * said to be the invention of an English physician of the name of Wright: the use of which was first introduced in England for smelting ores, about the end of the last century.”*

To describe the pearling Furnace in a more familiar manner:—The form of the body of it may be said to be very much like a baker’s oven, open on one side. The greatest extent of the hearth is in length six feet, in width four. The fire place and ash hole are on the side of the opening. The fire place is separated from the body of the Furnace by a partition wall, raised about two or three inches from the hearth, running along the whole length of the side. This wall leaves an opening of about four or five inches above it, for the passage of the flame to the body of the Furnace. The grates to support the fuel

* Macquire.

separate

separate the fire place from the ash hole, and should be sunk about six or eight inches below the level of the hearth.

Formerly the pearling Furnace was built with a fire place on each side ; but of late, the fire place on one side is found equally to answer.

The distance of the roof on the inside of the Furnace, from the hearth to its crown or highest part, should not exceed fourteen or fifteen inches.

It is usual to have two chimneys to the body of this Furnace ; one at the entrance, to receive the flame and smoke, when the door is open ; the other opposite to it, at the farthest end.

This Furnace has also two doors ; one at the fire place, about 12 inches wide, another at the opening at the front of its body, about 18 inches wide, and ten high ; through which the salts are thrown into it.

The fire is led to play throughout a well constructed Furnace, by three or four flues judiciously disposed around it, at the bottom of the wall, directly upon its hearth. These openings communicating with the chimneys, cause a draught which circulates the flame over every part of it.

P O T A S H F U R N A C E.

THE Furnace in use, for manufacturing Pot Ash, is of a different construction. It consists of two large iron boilers, or kettles, set in brick work,

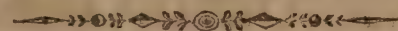
work, that will hold from 50 to 70 gallons, measuring about three feet over the top ; they should be very thick at the bottom to endure the fire, and provided with covers of plated iron. Under the kettles is the fire place and ash hole. At the mouth of the fire place is the door, at the farthest end of it is the chimney. The grates that separate the fire place should be sunk below the bottom of the kettles at a distance not exceeding 14 inches ; the width of the fire place door should be about 18 inches.

It is easy to conceive that by this construction, whenever the fire is urged so strongly as to produce a red heat in the kettles, and sometimes beyond it, that the draught from the ash hole will drive a great portion of the fire into the chimney, and even force the flame out at the top to a considerable height. This is what generally happens on *melting down*.

Being desirous to attend particularly to this operation, and aware of the inconvenience it must occasion, when performed in the town of Boston, where every blaze, out at the top of a chimney, excites an alarm, and subjects the proprietor of it to an expensive penalty ; I applied to Mr. Heath, an intelligent artist, an inhabitant of the town, to vary the construction of the Pot Ash Furnace so as to obviate this difficulty. He has effected the purpose completely. Instead of carrying out the chimney from the farthest end of the fire place, he there left a sufficient vacancy beyond the
kettles,

kettles, for the fire to pass up to the flues, which he opened, one on each side the kettles, to return the flame round them toward the mouth of the Furnace, and conduct it into the chimney raised directly over the door.

This improvement lessens the consumption of fuel, for by it, the same fire is brought to act a second time on the kettles, is nearly expended round them, and not wasted in the chimney.



POSTSCRIPT.

IT would be injustice to the remarks on the subject of Pot and Pearl Ashes, not to notice an advertisement which appeared in the Gazette of the United States, published July last, at Philadelphia, and signed Samuel Hopkins.

It is there asserted as an advantage arising from Mr. Hopkins's method of manufacturing Pearl Ash, that "by calcining the ashes before the leys are drawn from them, we obtain as great a quantity, at least of Pearl Ashes, as of common black salts;" and Mr. Hopkins adds, "Pearl Ashes generally sells, when at market £50 per ton. The highest price for black salts is £25 per ton, and if converted into Pearl Ashes, it requires as much more labour and fuel as in the first instance, and a loss from twenty-five to thirty per cent." Could this be realized, lucrative indeed would be the business. But if it should turn out that spurious ashes are the product of his supposed improvement; that they are the alkaline salt confounded with a variety of neutral salts, and a greater portion of earth than are found in Pearl Ash manufactured after the usual mode; although so bleached by the action of the fire and air, as to give it the appearance of good "Pearl Ashes of a very fine white colour;" yet when accurately analyzed, even the 25 or 30 per cent. supposed to be saved in the weight of the Pearl Ash, may discover itself to be still the earthy and saline impurity, although deprived of colouring matter by calcination.

If this is the result of Mr. Hopkins's method, it will not be deemed presumptuous to call in question his mode of manufacturing, although sanctioned by a patent, and recommended by the opinion of some of the most celebrated characters in the United States—characters justly celebrat

ed for their distinguished eminence in science.* In this instance, however, they appear complaisantly to have subscribed to *Mr. Hopkins's definition*, where he says, "Black salts are made by boiling down the leys from common wood ashes, until they are perfectly dry;" and "Pot Ashes are made by melting the black salts in a very strong fire, and ladling it out into coolers;" without the least intimation that from the alkaline salt all others are to be separated, to make the *best* of ashes:—For, in the alkali alone is the excellence of Pot or Pearl Ash. Indeed some have vainly imagined that by Mr. Hopkins's method of manufacturing, an actual *transmutation* of 25 or 30 per cent. is effected, and that the saline impurities are converted into genuine alkaline salt.

The gentlemen referred to, who gave Mr. Hopkins their certificate, could not entertain such an opinion; for, although *tartar* is alkalinized by fire, and *nitre* by the peculiar inflammability of its acid, when burned, leaves its alkaline basis uncombined, yet the strongest fire of a glass house has never effected the separation of the vitriolic acid from its alkaline basis in vitriolated tartar, or the marine acid from the mineral alkali in sea salt. By force of fire they may both be melted, and perhaps evaporated; but when dissolved, or condensed, they are found the same, and may again be chrysalized. No chemical fact is better known, or more thoroughly established, than that the union of acids and alkalies in neutral salts, is too strong to be in the least effected by any sort of earth yet known; therefore it is not to be expected that either the acid of neutral salts will be dissipated, or any new combination will take place in consequence of calcining them with the earth of wood ashes.

Mr. Hopkins also says, that "Pot Ashes made from calcined ashes are allowed to be much superior to those made in the common mode."

However fair the Pot Ash may be made to appear by the previous calcination, unless the neutral salts have been separated, it cannot be equally as good as that which is properly made, because it does not contain the same proportion of alkaline salt.

There cannot be a more decisive test to evidence this, than to take a specimen of each, and with the same ingredients, under similar management, to ascertain the quantity of soap they severally produce.

* David Rittenhouse, Benjamin Rush, James Hutchinson, Benjamin Say, Casper Wistar, jun. and John Pennington.

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FACTS

REGARDING THE DISINFECTING POWERS

OF

CHLORINE;

WITH AN EXPLANATION OF THE MODE IN WHICH IT OPERATES,
AND WITH DIRECTIONS HOW IT SHOULD BE APPLIED
FOR DISINFECTING PURPOSES :

5796.63

IN A LETTER FROM

CHESTER AVERILL, A. M. .

TO THE

HON. JOHN I. DEGRAFF,
MAYOR OF THE CITY OF SCHENECTADY.



Schenectady :

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1832.

CITY OF SCHENECTADY, July 3, 1832.

CHESTER AVERILL, Esq.

Dear Sir,

I perceive by the public papers that some doubts have been expressed respecting the disinfecting power of the Chloride of Lime.—At the present juncture, this question is evidently one of the highest interest. I beg leave, therefore, presuming that your professional pursuits have led you to investigate the subject, to request, that if consistent with your engagements you will furnish for the benefit of the public, any facts pertaining to this question which may be in your possession.

I am, dear sir, very respectfully,

Yours, &c.

JOHN I. DE GRAFF, *Mayor.*

UNION-COLLEGE, July 4, 1832.

*To the Hon. JOHN I. DE GRAFF, Mayor
of the City of Schenectady :*

Dear Sir,

THE present state of the public mind and of the public health, admonish me that I should waste no time in complying with the request contained in your letter of last evening; I shall therefore immediately avail myself of such opinions and facts as present themselves to me, in the discussion of the following questions :

1st. Has chlorine disinfecting powers ?

2nd. What is its known mode of operation in certain cases and its probable mode in others ?

3rd. How should it be applied for the purposes of disinfection ?

1st. HAS CHLORINE DISINFECTING POWERS ?

* "Les exhalaisons produites par les matieres animales en putrefaction, et meme par les individus attaques de certaines maladies, sont toujours plus ou moins dangereuses a respirer. Pendant long-temps l'on a cherche vainement les moyens de les detruire. Enfin M. Guyton nous en a fait connaitre un qui ne laisse rien a desirer. Il consiste a repandre, dans le lieu ou se forment ces exhalaisons, une certaine quantite de chlore gazeux."—*Thenard Traite de Chimie*, vol. 4. p. 694.

"Another important application of oxymuriatic acid (chlorine) gas, is that of destroying or neutralizing contagion."—*Dr. Murry's Chem.* vol. 2, p. 565.

"The remarkable power of chlorine, and its officinal compounds, chloride of lime and soda, in decomposing and destroying the fetid effluvia of animal and vegetable bodies in a state of putrefaction, has been so long known, has been verified in so many instances, and is susceptible of such direct demonstration, as to be beyond the cavils of medical pyrrhonism in its most wanton mood. That these effluvia are capable of making morbid impressions, upon the living body, is also placed beyond any reasonable doubt, not only by the sickness they instantly occasion, but by the many recorded cases of fevers of a putrid or low typhoid type, brought on by incautious exposure to masses of animal matter far advanced in putrefaction."—*Dr. Ure in the Jour. Roy. Ins.* No. 4, p. 83.

"Chlorine is by far the most powerful agent hitherto discovered to counteract contagion and all kinds of noxious effluvia and its sanative powers appear equally extraordinary."—*Dr. Silliman's Chem.* vol. 2, p. 68.

I have here quoted the opinions of eminently scientific men, at least three of whom are M. D's. and all of whom, it may be thought, do not deserve to be styled empyrics. But what weight ought these opinions to have in this discussion? Surely no more than those of any other person even much less eminent, unless they are better substantiated by facts. It was thought advisable, however, to quote them, since they may serve to correct any bias which entirely opposite opinions, proceeding from no higher source, may have occasioned.

*It is always more or less dangerous to respire those exhalations arising from animal substances in a state of putrefaction and even from individuals attacked with certain diseases. For a long time the means of destroying these were sought for in vain. At least M. Guiton made us acquainted with one which leaves us nothing to desire. It consists in evolving, in the place where these exhalations form, a certain quantity of chlorine gas.

But let us inquire what facts have so satisfactorily established, in the minds of our authors, men who have spent comparatively long lives in reflection and inquiry, the point that chlorine possesses those energetic disinfecting powers which they ascribed to it?

1st. FACTS OF PERSONS USING CHLORINE ENJOYING IMMUNITY FROM DISEASE, WHILE OTHERS NOT USING IT AND APPARENTLY EXPOSED TO THE SAME MORBIFIC OR INFECTIOUS AGENCIES, HAVE BEEN ATTACKED BY DISEASE.

The following is an extract from the letter of M. Parisot at the head of a medical expedition from France to Egypt and Syria, one of the objects of which was "to ascertain the effect of the chlorides on the infectious matter of the plague and on pestilential miasmata." The contagious nature of the plague was not doubted by him or those who commissioned him, it may be, for aught I know, by others.

—"We requested six sets of dresses (six shirts and six pair of drawers) in which persons had recently died of the plague; these, some of silk and some of cotton, were brought on the 2nd and put into the garden of the consul's house on the 3rd of June. On the 4th the state of the clothes was examined; they were foul with diseased matter and of a detestable odour. A woman (infected with the plague) steeped them in mere water to remove the excess of dirt, after which they were passed into a vessel containing a solution made by M. D'Arcet of six pounds of the chlorides in fifty lbs. of water, and there they remained 16 hours."

"On the 5th M. M. D'Arcet and Guilbau withdrew them from the solution, wrung them out and exposed them to the sun. The stains were weakened, but still very evident. At mid-day they were dry when each of us (there were six) took two pieces of the clothing and put them in contact with the skin. We put off this clothing on the 6th having worn it for eighteen hours. No one suffered; since then twenty-two days have elapsed and our health is the same."

D'Arcet, a colleague of Parisot, adds, that when "they wore the clothes next their skin they covered themselves up and took much exercise to excite perspiration. At this time from twelve to fifteen persons were dying per day—two hours after death a corpse was opened and examined; it was first

washed with chloride of lime and the hand kept continually bathed in the solution; the viscera were still warm. No injury to the examiners followed."

Inferences of Parisot "The consequence of all this is that we possess a means, 1st of disinfecting quickly and cheaply goods and clothing without the least injury to them. 2nd of reducing the disease to its own case and preventing it from producing a second or third case, and that by destroying the venom left in the first case which would otherwise perpetuate the evil; and not only can this be done with the plague but with the variola, rubeola, typhus, and even yellow fever.—*Ed. Jour. No. 13, N. S.*

"Two young medical men, desirous of examining a body which had been interred without dissection, in consequence of the prejudices of the relatives of the deceased, went in a very dark night to exhume it; but having mistaken the grave, laid open a coffin replete with such noisome corruption, that the gentlemen instantly sickened with the fœtor, were hardly able to go home, where they forthwith took to their bed, with symptoms of malignant fever and died. M. M. Orfila, Lessure, Gerdy and Hennelle, were employed about seven years ago, in Paris, to examine the body of an individual who was supposed to have been poisoned, and who had been dead and buried for nearly a month. Had they rashly proceeded to the inspection, they would most probably have fallen victims to their imprudence; the smell was intolerable and the body could hardly be approached; they had, therefore, recourse to the chloride of lime, sprinkling a solution of it over the putrid corpse, which produced, after a few aspersions, such wonderful effect, that the nauseous effluvia were instantly quenched, and the dissection was performed with comparative comfort."—*Dr. Ure, Sen. Jour. R. I. for Aug. 1831, p. 84.*

"Having performed several post mortem dissections of persons who have died from malignant fevers; dysentery with extensive ulceration of the mucous membrane of the large intestines, peritonitis with purulent effusion into the abdomen, hectic from suppuration, gangrene, &c. I have never suffered the slightest inconvenience. Yet these are the cases in which that peculiar animal poison is especially generated, which has occasionally proved fatal to the demonstrator of disease. I attribute the immunity I have enjoyed, in a great measure, to

my washing my hands immediately after each inspection, with the chlorosodaic liquor of Labarraque."

"A young gentleman, who acted as my colleague during part of last winter, but who did not adopt the above precaution, having imbibed, through a minute breach of surface on his little finger, a portion of this virus, was in a few hours thereafter attacked with acute inflammation of the absorbents of the arm, accompanied with high symptomatic fever, which confined him to his bed for many weeks, and required the most powerful antiphlogistic measures to subdue the inflammatory symptoms. I could cite instances of my predecessors having suffered from the same cause, but I deem it unnecessary as the fact is indisputable."—*Dr. Ure, Jun. House Surgeon of the Glasgow Royal Infirmary. Ibid. p. 83.*

"Several persons were bitten by a dog; some of these died with all the symptoms of hydrophobia, others were treated with chlorine; and though the symptoms returned once or twice on the early cessation of the remedy, yet they were vanquished by its continuance and a perfect cure effected."—*Dr. Previtali. Quart. Jour. vol. 12, p. 190.*

The following abstract from a letter by Mr. Dauvergne to M. Gay Lussac, giving a highly interesting illustration of the powers of chlorine, may with propriety be introduced under this head:

"Two drops of hydrocyanic (Prussic) acid were put into the end of a glass tube, and introduced into the lachrymal gland of a cat: contractions immediately came on, followed by strong tetanic convulsions, an abundant salivation took place, producing, through hard breathing, a thick white froth. The pulsations of the heart were quick, irregular and extensive, as if each were the last effort of life. Inspiration was difficult and painful; expiration frequent, prompt and forcible. Notwithstanding this desperate state of the animal, M. Simeon was induced, from his previous knowledge, to expect good effects from the use of chlorine, and therefore introduced a considerable quantity into the mouth; the salivation in consequence ceased; the respiration became easy; the circulation less forced and rapid. The animal now raised its head which before it could not do; put out its tongue and scented the chlorine as if it took pleasure in respiring a salutary and agreeable atmosphere. At the end of two hours, traces of the

event were scarcely visible.”—*Quart. Jour.* vol. 26, p. 421. *Vide also Jour. R. I. No. 1, p. 188.*—I might cite other facts under this head, but it is not deemed necessary.

2d. FACTS ILLUSTRATING THE POWERS OF CHLORINE IN DISINFECTING PLACES, WHERE ENDEMIC DISEASES HAD PREVAILED, OR WHERE THEY MOST PROBABLY WOULD HAVE PREVAILED, HAD IT NOT BEEN FOR THE AGENCY OF CHLORINE.

“I am acquainted with a very worthy company of Scotch bleachers, who have built several hundred cottages on their estate, for the use of their workmen and their families.”—“Whenever there is an appearance of fever in any one of these houses, one of the managers orders the whole family out of it—shuts up the house—having provided that every part of it may be completely filled with the chlorine gas, which quickly neutralizes or destroys all the putrid miasmata, and renders the habitation perfectly safe and wholesome.” For twenty years no fever had made any progress in that establishment.—*Parke’s Chem. Ess. Vol. 2, p. 345.*

“During the long period of thirty years that I have conducted this establishment, (where a great many tons of chloride of lime were for many years treated every week with sulphuric acid, in order to obtain a strong aqueous solution of chlorine) with a population of two or three thousand, including their families, I am not aware of a single case of disease that could be classed as contagious; and in many hundred cases in which I have recommended chlorine in the village, (Barrowfield) its good effects have been apparent in arresting the progress of the typhus and other fevers.”—*Mr. Rogers, Jour. R. I. No. 4, p. 96.*—“While typhus was prevalent in the neighborhood, none of the workmen employed in the manufacture of chloride of lime, were ever its victims.”—*Mr. White of Shawfield—ibid. ibid.*

James Corkindale, M. D. LL. D. physician to the goal at Glasgow, and celebrated for his skill in medical jurisprudence, writes regarding about twelve families, residing in the vicinity of works for the preparation of chloride of lime. “These persons have continued to reside there for various periods from two to twenty years. I examined the condition of these people, and made inquiries as the history of their health, during

their residence as detailed by themselves. I found that their condition, in this respect, was nearly the same as other persons of the same rank of life, in ordinary situations; but it was the uniform statement of the whole of them, that no person residing on these premises, had been affected with typhus at the different periods when that epidemic was very prevalent at Glasgow. It was evident, from inspection, that this immunity was not owing to superior cleanliness and ventilation, for the apartments were as dirty and as crowded as the ordinary habitations, where I know typhus had prevailed. The vapors from the works were various, but by far the most prominent was chlorine.—*Ibid.* 97.

“A letter from A. Chevalier to M. D’Arcet, (after the revolutionary struggle in July, 1830) informs the latter, that the writer in passing near the Morgue on the 30th, was forcibly struck with the putrid exhalations which issued from it, and which were very perceptible as far as the pont St. Michel. Fearing unpleasant consequences to the whole neighborhood, he sent one of his pupils immediately to the directors of the Morgue, to offer them, gratuitously, the use of as much chloride of lime as might be requisite to arrest the infection, which being accepted, and learning that they were about to remove, immediately about two hundred dead bodies that were heaped up in the Morgue, he proceeded, though without authority, to the place; prepared a large quantity of liquid chloride, and sprinkled it over the bodies, which, as they were moved, exhaled the most foetid odour. He persuaded the poor men who were employed in the work, though with some difficulty, to wash their hands every time they handled the bodies.—These, as they were taken to the boat, were well sprinkled, and portions of the dry powdered chloride were scattered in every place where it appeared necessary. These precautions, notwithstanding the mass of putrifying materials, completely overcame the exhalations, or these gave way to those of the chloride.”—*Quoted in Silliman’s Jour.* vol. 21, p. 149.

“The numerous and important applications that have been made of these two liquids, (chlorured compounds of Labarraque) in France, for the last three years, deserve the most earnest attention. By their aid, the purification of the tainted air in hospital wards, prisons, work-houses, lazarettos, ships,

sick chambers, closets, sewers, wells, drains, stables and manufactories, in which animal substances in a state of putrefaction are used, has been effected in the most satisfactory manner; and not only with greater ease, but in a much shorter period of time, than by any other method previously employed. Subsequent experiments have shown that these liquids may also be used with great advantage in arresting mortification or gangrene in the living body; and, it is probable that further applications of the utmost interest may shortly be published.

“In the hands of the physician, whose duties call him to the bed-side of patients labouring under infectious or contagious disorders; in those of the anatomist, whose pathological inquiries expose him to much risk and inconvenience; to the magistrate who has the salubrity of large and crowded communities intrusted to his vigilance—the disinfecting liquids have already been of the most essential service, accomplishing their respective objects with a success that no other method previously devised had ever ensured. These are *facts* that no longer rest on the mere dictum of a single individual.”—*A. B. Granville, M. D. F. R. S. physician in ordinary to the duke of Clarence. Quart. Jour.* 22, p. 372.

“The cathedral of Dijon had been, for several years, infested with a febrile fomes or miasma, which occasioned fever in many of its pious visitants, and it had become, in consequence, nearly deserted as a place of worship. Being then (1794) professor of chemistry in the academy of Dijon, M. Guiton was naturally induced to exercise his science in expurgating the air of the church. He accordingly filled the whole capacity of the building with muriatic acid gas, (a compound of hydrogen and chlorine) disengaged from a mixture of salt and sulphuric acid, distributed in a number of stone-ware dishes. The doors and windows were kept close for two or three days, to prevent the dissipation of the acid fumes. At the end of this period a free ventilation was given, after which the church was found to be deprived of its unpleasant smell and unwholesome effluvia.” Notwithstanding the successful result of M. Guiton’s experiment, with muriatic acid, he afterwards strongly recommended the use of chlorine for disinfecting purposes, and contributed much to its introduction.—*Dr. Ure, Jour. R. I. No. 4, p. 85.*

“On the 11th of July last, the fleet destined for the invasion of Mexico, conveying, in addition to the usual complement of mariners, a large number of soldiers, was overtaken in the Gulf of Mexico by a violent tempest, which continued for several days. The severity of the storm rendered it necessary to remove the windsails, and to close, not only the ports of the lower gun deck, but likewise those of the main deck, and to place on the hatches. In this condition of the ships, with such a crowd of persons confined together, in the middle of summer, within the tropics, without fresh air, putrid fever and malignant dysentery soon made their appearance.—The air is described as possessing, in addition to a highly offensive effluvium, an acrid heat, burning to the skin, with a degree of density that arrested respiration and produced giddiness.

“At this moment of distress and anxiety for the safety of all on board, the chlorine was used with the most decided and happy effects. Twelve vessels, containing one ounce each of the chloride of lime, in solution with water, were suspended on the birth deck, four were placed on the orlop deck, and in the gun room. In the space of two hours, the atmosphere lost all its deleterious qualities, and became perfectly agreeable, leaving nothing perceptible but the smell of tar, which always exists more or less in ships. The solutions were renewed every twenty four hours; but the chloride undissolved at the bottom of the vessels was then sprinkled on the decks, and thrown into such vessels as it became necessary to cleanse.—During the whole of the campaign, which lasted three months and a half, the atmosphere was preserved in this pure state by the chlorine, to which all the surgeons unite in attributing the very few instances of death that occurred in the fleet, when there existed such fruitful sources of fatal disorders.”—*Silliman's Jour.* Vol. 19, p. 165.

It seems to me that I need not farther accumulate facts under this head—that I need not speak in detail of numerous expurgations of infected penitentiaries, hospitals and ships—nor of the much diminished amount of sickness in prisons, on ship-board, and in unhealthy manufactories, at home and abroad, since chlorine has been habitually used in them. It seems to me that the number of experiments already detailed; the characters of the persons who made them, and the results

of those experiments, have rendered it unnecessary that "the use of chlorine" should, at present, be empirical—not founded in science, nor the result of deduction from observation.

3d. FACTS ILLUSTRATING THE SANATIVE POWERS OF CHLORINE, ITS ACTION UPON MORBID MATTER FROM WHICH ITS DISINFECTING POWERS MIGHT HAVE BEEN INFERRED.

"The chloride of soda has lately been most beneficially introduced into the materia medica. The chlorides arrest animal and vegetable decomposition. Chlorine acts chemically upon the morbid matter and resolves it into innocuous principles; the application of the chloride of soda in carbuncle, ulcers, gangrenous sores and mortification, and in cutaneous diseases, has been successful. It is used as a gargle in ulcerated sore throat."—*Silliman's Chem. vol. 2, p. 69.*

"Dr. Sacco of Milan, finding that two or three ounces of the solution of chlorine, might be drank at once without injury, and reasoning from its effect on infectious matter, administered it in cases of spotted fever, and found that in two or three days the effect was to reduce the disease to a simple fever, to shorten the period of its duration, and to lessen the diminution of strength, and other bad consequences that remain after the fever is removed. And from the constant good effect produced in these and similar cases, Dr. Sacco states his conviction, that it will be of the utmost service in the putrid fever, yellow fever, plague and all other contagious disorders."—*Quart. Jour. vol. 12, p. 190.*

"Dr. Brown employs chlorine, in solution, in cases of the scarlet fever, he says, with the utmost success. In the sore throat, sometimes accompanying the fever, it is more easily swallowed than mucilaginous drinks."—*Ibid. vol. 16, p. 395.*

"Prof. Ives successfully administered chloric ether in cases of severe paroxysms of pain in the chest, and difficulty of breathing, and of scarlet fever. He remarks that it is diffusible in its action like the other ethers, it possesses the peculiar properties of chlorine, and it has this advantage over other ethers, that it is always grateful."—*Silliman's Jour. vol. 21, p. 406.*

Now if there is ever a specific virus in the system, constituting or occasioning disease; and if the virus of the noxious exhalations therefrom is identical with or analogous to it, which may be thought highly probable, is it not fair to infer

that, if chlorine is found to destroy the virus in the system, it would also render innocuous its noxious exhalations?

I must confess, sir, that my reading on this subject has not been very extensive. I have not had access to many books which might have rendered me important instructions relating to this discussion; but I ask whether any man, free from prejudice, and willing to give the matter something more than a superficial examination, after having read the opinions with which this discussion commenced, and the three classes of facts which I have collated, with the authorities by which they are sanctioned, can doubt that chlorine possesses energetic disinfecting powers—that its use is not at present empyrical—but *is founded in science, and is the result of deduction from observation?* I have not sought to prove that chlorine can destroy the particular infection, if it be infection, that causes the cholera, I am confident that I could have satisfied neither myself nor any one else had I so sought, but I have sought to convince all of what I firmly believe, that chlorine may be employed with great advantage as a disinfecting agent, in all cases where disagreeable or morbid exhalations arise from the decomposition of vegetable and animal substances, and that *at the present juncture it ought to be considered indispensable in and about every house in our populous cities.*

The following letter to Dr. Ure from M. d'Epinay, agent of the island of Mauritius, to the British government was not introduced under the first class of facts where it might properly have been referred, because I was desirous of collecting facts to prove the general rather than the particular disinfecting powers of chlorine, and because the facts detailed in the letter may be thought not to prove any thing conclusively.

I cannot refrain, however, from inserting it in this place. "I told you that in the Isle of France, during the cholera, we employed as a disinfector a mixture of oxide of manganese and muriatic acid, (materials by whose action chlorine is evolved) We provided small phials of it, which were carried about in all the infirmaries, and by the people who entered the hospitals. They were also carried about by the women and children; and it was remarked that none of those so protected by the disinfecting phials were attacked by the disease."—*Jour. R. I. No. 4, p. 100.*

The following notices from the London Sun have just come to my hand and are deemed of the very highest moment:

"We stated some time ago that in consequence of a letter from A. R. Raeburn, Esq. of St. Bernards, the board of health of Musselburgh, adopted the plan of fumigating the streets, lanes, alleys and houses there with chlorine raised from sea salt and manganese by means of sulphuric acid; and it is worthy of remark, that from the commencement of this operation, the disease rapidly diminished in number of cases and in virulence, so that in eight days it had entirely ceased in Fisher's row, and the instances of it have been very few even in the Musselburgh district. But what happened in Porto Bello is probably still more conclusive. The Cholera had just begun to rage in that village; from the 17th to the 18th ult. there were seven deaths and several cases considered dangerous.—The board of health then adopted the plan of public and private fumigation, which was most thoroughly done, and the malady seems to have been subdued or rather extirpated in one day. Porto Bello has had no new cases since the 23d and no new deaths except one on the 25th."

But the Cholera has been so unexpected in its arrival in certain places and so sudden in its disappearance from them, that these experiments may, to many, appear inconclusive.

2nd. WHAT IS ITS KNOWN MODE OF OPERATION IN CERTAIN CASES AND ITS PROBABLE MODE IN OTHERS?

* "Le chlore attaque presque toutes les substances vegetales.—L'action a lieu a la temperature ordinaire; c'est toujours en s'emparant d'une partie de leur hydrogene qu'il decompose ces substances: il passe ainsi a l'etat d'acide hydrochlorique, et les transforme en d'autres matieres qui n'ont point encore ete examinees. Peut-etre au nombre de ces matieres doit-on placer l'acide carbonique, l'acide acetique; peut-etre aussi sont-elles nouvelles.—Il est facile de concevoir, d'apres cela, pourquoi l'on emploie le chlore avec tant

*Chlorine acts upon nearly all vegetable substances. The action takes place at the ordinary temperature. It is always in combining with a part of their hydrogen that it decomposes these substances; it thus passes to the state of muriatic acid, and changes them into other substances which have not yet been examined. Perhaps among the number of these substances we should place carbonic acid, acetic acid; perhaps also they are new. It is easy to conceive, from this, how we employ chlorine with so great success for the decomposition of the putrid miasmata which sometimes become diffused through the air.

de succes—et pour decomposer les miasmes putrides qui se repandent quelquefois dans l'air.—*Thenard, Traite de Chimie tome 3d, pp. 579-80.*

“Mr. Faraday confined himself (in a lecture before the Royal Institution) to considerations purely chemical. Chlorine acts upon putrid or infectious miasmata, sometimes by the abstraction of hydrogen, with which it forms muriatic acid; sometimes by combining with and forming triple compounds with the carbon and hydrogen of the vapors; and sometimes, perhaps, by evolving oxygen which, in its nascent state, acts upon the effluvia; but in all cases it acts chemically, and converts that which is noxious into inoffensive substances.”—*Quar. Jour. vol. 22d, p. 461.*

“The phenomena of putrefactive fermentation seem to show that the fetor resides in certain hydrogenated compounds containing carbon, sulphur, phosphorus, azote, &c.; for gaseous matter of this kind is eventually disengaged in the larger cavities of the trunk, as well as in the cellular tissue causing a general intumescence. There is every probability, likewise, that the diffusible fomes of contagious disease resides in some analagous compounds, but of so subtle a nature as hitherto to have baffled every effort of chemistry to collect and analyze.”—*Dr. Ure, Jour. R. I. No. 5th, p. 85.*

Dr. Ure, doubtless, considered that the strong affinity of chlorine for hydrogen, and the change of the nature or properties of a compound resulting from a change in the proportion of its elements, were so generally known as to render it unnecessary that he should be particular in specifying the mode, in which chlorine acts as a disinfectant. You cannot but have marked the emphasis with which he asserts the probability that the fomes of contagious disease resides in certain compounds analagous to the hydrogenated compounds specified by him.—He knew that it is entirely unphilosophical to affirm that the principle of contagion is not a compound gas, in many respects such as chemists are accustomed to catch in their receivers.—It may be, for aught that is known, some compound of sulphur and hydrogen, or of carbon and hydrogen or of hydrogen and nitrogen, or of any other known or unknown elements, possessing extreme tenuity, and having its elements combined in different proportions and by different laws, from those of any known compound. The principle of contagion is, as yet, only

known to exist by its action upon the animal system, and its chemical constitution is only inferred from the well attested agency of chlorine in destroying it. Chemists as well as others are liable sometimes to deduce too general inferences from particular facts; but there have been so many facts illustrating the action of chlorine upon contagious or infectious matter, as to lead them to conclude, that most if not all virus of vegetable or animal origin contains hydrogen which can be abstracted by the action of sufficient free chlorine, and thus the virus destroyed. Whether it be always, or in what cases, it is practicable to administer the quantity requisite to destroy virus when in the system, are questions foreign to the present discussion. From what has now been said however, it is easy to conceive how chlorine acted when administered to those who gave symptoms of hydrophobia, and to the cat, in which it proved an antidote to Prussic acid. But however the truth or justness of inferences from well attested and well understood facts, employed in the explanation of other facts, may be disputed, the facts themselves, which these inferences were intended to explain, should not, on that account, be discredited.

The utility of many things has been accidentally discovered, and we have long availed ourselves of their use without having been able to explain the peculiar relation which they sustained to our necessities or conveniencies, or what particular changes they effected in us, or in that which concerned us. It has not been so with chlorine. Occasions for its use have been pointed out, and the mode of its operation has been explained by science. There has been less blind experiment with it, than with, perhaps, any other agent that has contributed to our health and comfort.

It may be important to speak in this connexion of various other means often used for disinfection and to discriminate between the mode of their operation and that of chlorine. These are the kindling of fires, discharging of cannon and musketry, burning of sugar, tar, sulphur, the fumes of vinegar and camphor, &c. When the infected air occupies low and confined situations, where ventilation is difficult and imperfect the three first mentioned means may be employed perhaps with much advantage: not by destroying the infection, but by dissipating it—by creating currents in the air which would bear away some of the foul air, and introduce some that

is pure. In respect to the five last mentioned means, they could produce this effect only in a very slight degree and, there are no facts or analogies to render it probable that they destroy infection by acting chemically upon the matter of it. The only good effect which they can have, is to render fetid substances imperceptible to our sense of smelling, by themselves affecting it with greater pungency than the fetid gases. They serve to disguise, not to dissipate nor to destroy. And some of them are themselves positively deleterious. None of them should ever be depended upon where chlorine can be applied.

3rd. HOW SHOULD CHLORINE BE APPLIED FOR PURPOSES OF DISINFECTION ?

The most favorable mode of its application for these purposes, varies greatly, with the amount of infection and with the extent and numerous other circumstances of the place to be disinfected.

The following observations are from Mr. Faraday's account of a successful fumigation, with chlorine, which he gave to the general penitentiary, at Millbank, England.

"I was desirous for many reasons of obtaining a gradual and successive developement of the disinfecting agent, rather than a sudden and short one. The latter mode, though it would have filled the building at once, and probably very effectually, yet would have seriously incommoded the operators, and would also soon have disappeared in consequence of absorption by the limed walls, and from dissipation through apertures that would inevitably remain unclosed in different parts of the building; whilst the former mode, by continually supplying the disinfecting agent to the atmosphere of the place for a length of time, would enable it better to act on the bedding, clothing, and other articles left in the cells, and allow it also more perfectly to penetrate to every part of the building itself.

"The materials used were common salt, oxide of manganese in powder, and oil of vitriol. I found that a mixture of one part by weight of common salt and one part of oxide of manganese, when acted upon by two parts of oil of vitriol, previously mixed with one part (by weight) of water, and left till cold, produced the best results. Such a mixture made at the temperature of 60 deg. Fah. liberated no muriatic acid; but

in a few minutes began to evolve chlorine and continued to do so for four days. When examined on the fifth day and urged by heat, so as to cause the liberation of all the chlorine that could be afforded by it, only a small proportion was obtained. Such a mixture therefore may be considered as having liberated its chlorine gradually but perfectly, without the application of any extraneous heat, and it is therefore very proper for extensive fumigation.

“The vessels in which the mixture is to be made should be flat, and such as, being economical, are least acted upon by the chlorine or acid. Common red pans were used—better earthen ware would have been too expensive.

“Preparatory to the fumigation, a quantity of the salt was turned out, the lumps broken down by a mallet until the whole was in powder, and then an equal weight of the oxide of manganese added, and the whole well mixed. The acid and water were mixed in a wooden tub, the water being put in first, then about half the acid added, stirring at the same time.—When the heat produced had been dissipated, which happened in a few hours, the rest of the acid was added, stirring as before, and the whole left till cold. The men used measures in mixing the acid and water; and were told to take rather less of water than of the acid, 9 measures to 10 being nearly the quantities required. Any slight departure from these proportions would be of no consequence. The pans were then charged with the mixed manganese and salt, and with the dilute oil of vitriol, so as to form the mixture first described, and were distributed at proper intervals along the galleries, &c. doors, windows, key-holes, &c. having been cautiously closed. The mixture was well stirred with a stick, and left to itself. This was done without inconvenience to the operators, except when the dilute acid was applied, before it had cooled, to the mixture of salt and manganese; there was abundant time to go from pan to pan and to close the various galleries in succession.

“The whole quantity of materials used was 700 lbs. of common salt, 700 lbs. of oxide of manganese, and 1400 lbs. of oil of vitriol. The space requiring fumigation amounted to nearly 2,000,000 cubical feet, and the surface of the walls, floors, ceilings, &c. exclusive of furniture, bedding, &c. was about 1,200,000 square feet. This surface was principally stone and brick, most of which had been lime washed—the

means employed were applied, to an extent probably far beyond that requisite to the destruction of any miasmata that might be within the penitentiary. I should consider from one half to one fourth of the chlorine evolved quite sufficient for any of the usual cases where fumigation is required.”—*Quart. Jour.* vol. 18, pp. 92-5.

This mode of applying chlorine is the most economical and the most favorable in disinfecting lanes and alleys in cities, and public and private buildings when they are not occupied; the amount of materials employed always bearing a proper relation to the extent and condition of the place to be disinfected. It may often be desirable to have a more prompt effect or to have a fumigation completed in less time than was employed by Mr. Faraday: in such cases the process may be much hastened by the application of heat to the vessels containing the materials.

But there are many places, which require to be disinfected, to which this kind of fumigation cannot be applied. There is need, therefore, of further instructions and I here subjoin some given by Dr. Ure, relative to this topic.

“As gaseous chlorine, in the state in which it is evolved from muriatic acid and manganese, has been thought to be too concentrated for diffusing, in apartments occupied by the sick, recourse has been had in a variety of cases, to the exhalations that spontaneously arise from chloride of lime, exposed in an extensive surface, either in its pulverulent form or dissolved in water. It is true, indeed, that under both of these forms the chloride exhales its peculiar odour, but it gives out no appreciable or operative portion of the gas.—Nothing, therefore, can exceed, in absurdity, the fashionable nostrum for disinfecting apartments, *charged with contagious fomes*, by placing in them one or more saucers filled with the chloride of lime.

“It has been supposed that the carbonic acid present in the air, displaces the chlorine from the lime, but after passing a current of this gas (carbonic acid) for a whole day, through the chloride diffused in tepid water, I found the liquid still to possess the power of discharging the colour very readily from litmus paper.—To pretend, therefore, to suffocate the hydra of contagion by subjecting it to the simple smell of chloride of lime in a saucer, is just such a mockery as it would be to appease the famished stomach by the smell of the cook

shop. The subtle effluvia of a pestilence must be combated by more energetic means, they must be environed with an atmosphere of chlorine adequate to effect their destruction. Every thing short of this consummation is paltering with the safety, not of a few individuals, but possibly of a nation. *Whenever chlorine has failed to extinguish infectious fomes, the operator, and not the chemical agent itself, has been in fault.*

“An apartment may be conveniently disinfected by placing on a shelf or support near the ceiling a small basin or pipkin, containing chloride of lime, having set over it a glass or earthen-ware funnel with muriatic acid, diluted with about its weight of water; the beak of the funnel being *partially closed with a cork so that the acid may drop slowly down on the chloride.*—Eight ounces of good chloride thus treated with ten ounces of muriatic acid, will suffice to fumigate and sweeten the air of a common sized chamber. *In applying chlorine gas to apartments, we should always bear in mind, that it is one of the heaviest of elastic fluids, and therefore it tends to occupy the lower region in preference to the upper.*”

Dr. Ure's instructions were given under the apprehension of a visit from the cholera in Scotland, and probably on that account he was more solicitous to prevent people from trusting to the exhalations that spontaneously arise from the chloride of lime, than he otherwise would have been. But altho' his language, concerning the inadequacy, of those exhalations, to the purposes of disinfection, may be rather too strong to be sustained by all facts; (vide the account of the disinfection of the ship, *p.* 11) yet important hints should be taken from it, relative to the degree of concentration, in which chlorine may safely be used and sometimes, perhaps, must be used to be effectual.

It is hardly necessary to remind those who have charge of sick chambers, that it may sometimes be important, to have the atmosphere of an apartment continually more or less impregnated with chlorine; and that, therefore, caution should be observed to renew from time to time, as it may be needed, a supply of the materials for evolving chlorine. As the proper frequency of renewal will vary with the kind of materials employed, and of infection to be destroyed, of course no general rule can be given.

Muriatic acid may not always be at hand when it is de-

sirable to disengage chlorine from the chloride; in such cases, and, indeed, in all ordinary cases, vinegar may be substituted for it, and disinfection effected, in the following manner:

For an apartment of ordinary size, dissolve half an ounce of dry chloride of lime in a gill of water, add half a gill of good vinegar, stir well the mixture, place it in a shallow vessel, (a saucer or a soup plate) situated near the ceiling of the room.

If the apartment be large, two or more vessels (according to the size of the apartment) supplied in this way, should be arranged in different parts of it.

It is not thought advisable to make this mixture even in bottles, before it needs to be used.

Attendants upon the sick should sprinkle some of the mixture in vessels containing impurities, and on the cloths which may be used to cover them.

When there is no apprehension of danger from contagion, and the sole object is to destroy fetid gases, a bare solution of chloride of lime in water, will often be found to effect the object.

In such cases, dissolve half an ounce of the chloride of lime in about three pints of water and occasionally sprinkle the mixture around the apartment, and in the vessels as before directed.

When it is desirable to destroy the effluvia from drains, sewers, &c. or to purify the water of a cistern—dissolve about eight ounces of the chloride of lime in a pail full of water, and disperse it into them. *Repeat the operation until the object is effected.* Advantage may often be derived from scattering, into the place to be purified, a small quantity of hay or straw, and from sprinkling the solution over it.

It may be well to suggest to those who wish to keep the chloride of lime in their families, that it is important to preserve it in well stopped bottles or jars; since, when exposed to the air, "it rapidly passes into a deliquescent paste, consisting of muriate of lime and lime with an obscure displacement of oxygen," and its disinfecting purposes are thus destroyed.

If persons have to pass through lanes, or into infirmaries or hospitals, where great danger is to be apprehended from infection, they are advised to carry about them disinfecting phials

of the kind mentioned by D'Epinay, which may be prepared in the following manner :

Take phials of a convenient size (say ounce phials) having glass stoppers not very accurately ground; put into them about a tea spoon full of powdered oxide of manganese and about twice as much strong muriatic acid. The materials having been mixed by shaking the phials, will immediately begin to evolve chlorine, which will slowly escape between the stopper and the phial.

The directions and hints that have now been given, are thought to be sufficiently full and particular. When persons have become acquainted with the nature and use of chlorine, applied agreeably to those directions, any change in the mode of applying it, rendered necessary by peculiar circumstances, will readily suggest itself.

I should close this communication here, were it not to be feared, that, after all that has been written concerning the disinfecting powers of chlorine, persons may be apprehensive lest injury should result to the sick from the use of chlorine, and therefore refrain from using it.

On this topic it might be sufficient, to refer to what has been said relative to the health of those engaged in the preparation of chloride of lime, (vide p. 8) and to state that the respiration of dilute chlorine gas has been followed with success in cases of diseased lungs. But certain remarks of Dr. Ure are so apposite to this place, that I shall venture to insert them:

“But I shall be asked, whether chlorine gas can be diffused through the air of a chamber without injuring the lungs of living beings, as well as the furniture and goods? I answer yes, when it is distributed on philosophical principles.—But I might ask the medical practitioner, in return, whether the corrosive sulphuric and nitric acids, may be administered internally? Yes, he would be ready to reply, when sufficiently diluted; and the same answer will serve for chlorine. I have been a frequent inmate of manufactories of chloride of lime on the greatest scale, and I have occasionally found the atmosphere, in certain departments of the works, to be impregnated, in a sensible degree, with chlorine gas. Moist litmus paper would have speedily lost its colour in such an atmosphere, although dyed woollen and calico stuffs, in the dry

state, suffered no perceptible change. The workmen who habitually respired this chlorified air, experienced no evil effects on their health, nor, indeed, any inconvenience at all, unless an accident befel some joint of their apparatus. These facts prove the safety of immersion in chlorine largely diluted with air, yet still strong enough to blanch moist litmus paper, which may be regarded as a satisfactory criterion of its activity when directed against contagion."—*Jour. R. I. No. 4, p. 88.*

Hoping that this very hastily prepared communication, may be of service to the public, and meet with your approbation, I subscribe myself,

Very respectfully,

Yours, &c.

C. AVERILL.

1867
F. H. Brown

Mar. 17, 1866.

TECHNICAL CHEMISTRY.

6. *Disinfectants*.—The use of a mixture of coal-tar and plaster-of-Paris for purposes of disinfection and for dressing wounds, as proposed by CORNE and DEMEAUX (*Comptes Rendus*, xlix, 127; see this Journal, xxviii, 425), has been recently reported upon in the French Academy by a committee—Chevreul, J. Cloquet, and Velpeau (*rappor-teur*)—to which the subject was referred in July, 1859.

The great interest, which this method,—so favorably commented upon by the distinguished surgeon Velpeau soon after its publication,—excited among the medical men of France gave rise to the publication of numerous other systems of disinfection, which being submitted to the Academy for its approval were also referred to the committee in question. The labors of its members have thus been materially increased, and their report swelled to the dimensions of a general treatise upon disinfectants—especially those applicable to wounds.

In numerous experiments made at the Hospital *de la Charité* the mixed coal-tar and plaster of Corne was employed, both in the state of powder and as a poultice made by mixing it with oil. When applied as a thick layer, three or four times a day, upon putrid, gangrenous and sanious wounds, the powder destroyed their odor without giving rise to any special pain. Upon indolent sores, however, or upon recent burns,

the contact of the powder produced considerable smarting upon some patients, though well borne by others. Wounds of the first class were often found to be cleaned as well as disinfected; while those of the second class generally acquired a dirty, pale, gray tint, their cicatrization being hindered.

The poultices were found to be more advantageous than the powder in the treatment of cavernous wounds, purulent or fetid, and sinuous foci, open suppurating abscesses, anthracoidal suppurations, etc.

Applied directly to the sore, the poultices destroyed the putrid odors, allayed the inflammation without augmenting the pain, leaving beneath them a healthier pus, and the surfaces in better condition. In a word, the mixed coal-tar and plaster, when properly applied, disinfects wounds and putrid suppurations. As for the absorbent and detergent qualities which its inventors also claim for it, these are less clearly evident.

The powder absorbs better than the poultices,—the latter, it is true, take up a portion of the morbid exudations, but unless the dressing is carefully renewed, five or six times a day, pus will nevertheless collect beneath it. From this it follows that after having been somewhat cleansed the wound ceases, at the end of a few days, to clean itself, or to heal more rapidly than it would with the usual topical applications.

Upon ulcerated cancers, the mixture, either as powder or poultice, disinfects them partially, but neither dries up the suppuration nor alleviates the pain.

It is in the dissecting-room, upon organic matter in a state of putrefaction, that the mixed coal-tar and plaster is all powerful. The most infectious masses, when imbued with the powder, or simply rolled about in it, lose at once their disagreeable odor. According to Velpeau, his autopsy room was as approachable towards the close of last summer as it had formally been repulsive. It was freed from flies and other insects, as well as from putrid odors.

Although it would have been out of the province of the committee to experiment upon the application of this mixture in disinfecting filth upon the great scale, they have nevertheless proved that it can be advantageously used in hospitals for deodorizing urine or fecal matters.

The following inconveniences, to which the use of the mixture in surgery would give rise, are enumerated:

It not only soils the clothes of the patient, but hardens them and causes them to weigh more heavily upon or about the wound; it imparts to the bandages, with which the poultices are covered, a very tenacious rusty or yellow color; it must be frequently renewed, and although it destroys putrid smells, it retains a bituminous odor by no means agreeable to many persons.

These inconveniences are of comparatively slight importance, it is true, and may possibly admit of being remedied.

Of the other disinfectants submitted to the committee, several were only modifications of that of Corne and Demeaux:—Vegetable tar, as shown by Renault, may be substituted for coal-tar.—A mixture composed of hydraulic lime and tar did not disinfect wounds to which it was applied, nor could it be supported by the patients. With regard to the assertions of some practitioners, that common earth, talc, flour, or other

vegetable and mineral powders—even poudrette—when mixed with coal-tar furnish a more convenient and less costly disinfectant than that prepared with plaster, the experiments of the committee have proved that while coal-tar, mixed with common earth, well dried, or with sand, is equally, or perhaps much more, efficacious for disinfecting fecal matter as when mixed with plaster; that while comparative experiments made from this point of view upon sulphate of lime, clay, charcoal, linseed meal, and earth have resulted in favor of the latter, the same is by no means true in surgery. When applied to wounds or infectious suppurations these different mixtures were only partially successful, having proved to be less efficacious than the mixed plaster and coal-tar. In like manner the proposal to use an emulsion of coal-tar and tincture of saponine has not been found advantageous in practice: most patients complained of it, their wounds exhibited scarcely anything satisfactory, while the disinfection was very imperfect. The mixture of plaster and coal-tar was substituted for it, upon the same wounds, with decided advantage.

Although the modifications of Corne and Demeaux' process have not been particularly felicitous thus far, they have nevertheless served to confirm the fact that in reality it is the coal-tar which acts the principal part as disinfectant in these various mixtures.*

Among the numerous other substances proposed as disinfectants, or for dressing wounds, the following have not afforded satisfactory results:

Chlorate of potash,—mixed with clay or kaolin (for example, 10 parts of chlorate to 90 parts of white clay or fine sand) which was proposed as an absolute disinfectant, neither disinfected nor absorbed the pus of fetid wounds. The mixture would be in any case much more costly than coal-tar and plaster and certainly less efficacious.

Whites of eggs,—mixed with chalk and applied to wounds, previously oiled, succeeded no better than simple-cerate.

* The inefficiency of sulphate of lime as a general disinfecting agent when used by itself may be readily demonstrated by the following experiment which is of interest in view of the fact that a belief in the utility of gypsum as a deodorizer appears to be widely spread among recent writers. For that matter we are told by Paulet (*Comptes Rendus*, xlix, 199) that during the last 25 years more than fifty authors of processes of disinfection have announced, each as he believed for the first time, the use of plaster as a means of disinfection.

If a mixture of about equal volumes of powdered gypsum and fresh urine be introduced into a small phial, the mixture placed in a warm room and thoroughly shaken several times a day until the urine has become putrid, it will be observed that an exceedingly disagreeable odor will be developed, differing from that of ordinary stale urine inasmuch as it is unalloyed with the odor of ammonia. For the complete success of this experiment it is important that a large excess of sulphate of lime should be present and that the mixture should be frequently agitated, else the whole of the carbonate of ammonia will not be decomposed and will tend to mitigate the fetor of the special odor of the putrid urine. So far from disinfecting in this case the sulphate of lime really destroys a deodorizing, or at least a masking agent, ammonia; leaving free,—purified as it were, and unadulterated, an odor, the peculiar offensiveness of which is remarkable. Sulphate of iron being substituted for gypsum in this experiment afforded a somewhat similar result, although the odor obtained was a trifle less insufferable than that of the experiments with sulphate of lime. It should be here mentioned that the odors in question were in no instance contaminated with sulphuretted hydrogen,—as was ascertained by careful trials.

F. H. STORER.

Powdered sugar.—When employed in layers upon ulcers forms crusts, beneath which the suppurations accumulate and hinder the process of healing.

Cherry-laurel water, glycerine and cellulose.—According to Antier, glycerine mixed with equal parts of cherry-laurel water forms a valuable absorbent or disinfectant to be applied as a lotion or injection. This mixture converted into pomade by mixing it with powdered almonds was also proposed as a topical application for all kinds of wounds. But in the hands of the committee neither the liquor nor the pomade by themselves or mixed with kaolin produced any effect more marked than that of lead-erate and other anti-putrid or detergent solutions already in use.

The members of another group of disinfectants are worthy, in various degrees of consideration.

Among these charcoal appears in the front rank.—Surgeons have long regarded it as one of the best antiseptics known. Confined between pieces of linen according to the process of Malapert and Pichot it is more readily applied than when used as powder directly upon wounds; but the mixture of coal-tar and plaster, which disinfects still better and is more cleanly, is susceptible of a simpler and a more general application.

Coke of Boghead coal,—in powder as proposed by Moride* like carbon

* In view of the claim of Moride (*Comptes Rendus*, xlix, 242) as well as from its general interest the following extract from a report made to the British Secretary of War by Lewis Thompson (*London Journal of Gas Lighting, Water Supply and Sanitary Improvement*, 1856, v, 11) may here be cited.

Mr. Thompson states that he has instituted a set of experiments having a purely money basis as their exponent.—The articles enumerated were each employed until they practically deodorized one uniform quantity of the same mass of putrid sewage and the money value of the proportions thus used was deduced either from a broker's price-list or, where this failed to give the requisite information, by special inquiry from a wholesale dealer. The amount of sewage operated upon in each experiment was half a gallon taken from a single tank which had been recently filled out of a large and very offensive ditch or open sewer. Two indications of the progress of the disinfection were had recourse to in these experiments; one with paper dipped in sugar of lead which gradually ceased to become brown as the deodorizing agent was added in successive portions; the other had reference to the discontinuance of any offensive smell; and the attainment of this last condition was regarded as the termination of each experiment.

By this means he was enabled to draw up the subjoined table which shows at a glance the comparative cost of executing the same amount of deodorizing work with each agent on the supposition that Boghead charcoal can be had at the rate of \$3·00 [= 12s.] per ton.

Table showing the cost of Purifying one uniform Quality of Feculent Sewage by the several Articles mentioned.

Boghead charcoal (coke),	\$3·00
Nitric acid,	8·50
Black oxyd of manganese,	9·25
Chlorid of lime,	10·75
Peat charcoal,	11·00
Subchlorid of iron (imperfect),	11·25
Animal charcoal,	16·75
Chlorid of manganese (imperfect),	17·50
Bichlorid of mercury,	18·00
Impure chlorid of zinc in damp powder,	26·00
Chlorid of zinc in solution as patented by Sir Wm. Burnett,	37·00
Sulphate of copper,	39·00

The sulphates of zinc, iron, and alumina; common gypsum; sulphuric, sulphur-

when employed comparatively with coal-tar and plaster, alternately upon the same patients, proved to be less efficacious, less convenient and more disagreeable than the latter.

Mixed plaster and charcoal,—proposed by Herpin of Metz, irritates the wounds, disinfects badly, and soils everything it touches.

Carbonic acid,—proposed by the same author, appears to the committee to be too difficult of application in practice, though theoretically founded upon important analogies.

Bituminous Water of Visos—proposed by Manne, and the mud of rivers used as a poultice by Desmarts, do not appear to be susceptible of being substituted for the mixture of Corne and Demeaux.

The following substances have long ago acquired a place, each in its own way, in the class of disinfectants.

Tincture of iodine has been employed as an antiseptic by hospital surgeons since 1823. By modifying the surfaces to which it is applied, it usually improves the appearance of the pus, lessens its acidity, and is, to a certain extent, antagonistic to putrid infections. It disinfects, however, only incompletely, causes severe pain when applied to open wounds, and would be expensive if used on a large scale; finally, the odor of iodine is neither agreeable nor unattended by inconveniences.

Perchloride of iron has been used for some twelve years in hospitals as an antiseptic and as a means of modifying certain wounds, and putrid or sanguineous foci.—Without diffusing the disagreeable odor of tincture of iodine, it has, like the latter, the fault of disinfecting badly, of causing much pain, and of acting violently upon the diseased tissues, besides injuring the cloths which are soaked in it even more than is the case with the coal-tar and plaster.

Both iodine and the salt of iron just mentioned, are in fact agents of another order; they have rendered, and do still render important services. They are certainly well worth preserving, but should not be compared with the mixture of coal-tar and plaster.

Nitrate of lead,* *Creosote*, and other substances which have been proposed at one time or another, have not realized the expectations of their inventors; their price has been too great, their employment required too much care, or their action has not been sufficiently certain that they could be advantageously used in practice. There is, nevertheless, one of these which deserves special mention, viz., *chlorine*. Ever since Guyton Morveau demonstrated the true action of muriatic acid upon putrefying animal matters, the efficacy of chlorine has been tested in almost innumerable ways. Solutions of chlorine, of "chlorid of soda," and of "chlorid of lime," have rendered signal services to medicine and in the cause of public

ous, and muriatic acids; peroxyd of iron, highly dried clay, litharge, and saw-dust were found imperfect even when very large quantities were employed.

Arsenious acid and creosote on the contrary, were very active; but the danger of a subsequent evolution of arseniuretted hydrogen in the first case, and the difficulty of diffusing an oily fluid like creosote in the second, seemed to interdict the use of these substances.

F. H. S.

* [An excellent, though somewhat expensive "disinfecting fluid" (Ledoyen's), which was quite extensively used in this country a few years since, consisted, according to analyses of F. E. Holyoke, of an aqueous solution of this salt.—F. H. S.]

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health, especially since Labarraque, some thirty years since, indicated an improved method of employing them. But the odor of chlorine, disagreeable in itself, is neither easily borne nor devoid of inconveniences. Wounds, moreover, hardly accommodate themselves to it any better than the sense of smell, whenever somewhat large doses of it are required.

Chlorinated Sponge.—The idea of applying sponges saturated with chlorinated solutions, directly upon purulent or gangrenous wounds, as suggested by Hervieux, appears to be excellent for certain cases. Such sponges, renewed several times per day, absorb the pus gradually as it forms better than anything else, and disinfect the wound very well. Unfortunately, chlorine rapidly alters or destroys the sponges and soon causes undue irritation. While this method, therefore, is an excellent one for cleaning certain gangrenous and sinuous wounds, it is, nevertheless, inferior in most instances to the mixture of coal-tar and plaster.

Subnitrate of bismuth—suggested by Frémy as an absorbent and disinfectant, was applied to a large number of wounds. Upon large cavernous cancers it disinfected somewhat better than Peruvian bark, charcoal, or chlorate of potash, but less than the coal-tar and plaster. By its use, however, several bad looking wounds were cleansed quite rapidly. Since it causes no pain or irritation, and since it neither soils the skin nor the clothes, the subnitrate of bismuth is preferable to a multitude of other antiseptic powders; but it is useful rather as a solidifier (*incarnatif*), or dryer, than as an absorbent or disinfectant.

In their *résumé* the committee affirm:

I. That coal-tar mixed with plaster, according to the formula of Corne, (see this Journal, xxviii, 426), can disinfect putrefying organic matters. Mixed with alvine dejections this powder destroys their odor, and leads one to hope that by its aid profound reforms in the present system of maintaining and clearing out cess-pools, &c., may some day be brought about. For this purpose, ordinary earth, coal-ashes, or sand may be substituted for the plaster, as Cabanes prefers, being at least equally efficacious.

II. In therapeutics the coal-tar and plaster has fulfilled only a part of its promises. As a disinfectant in the dissecting-room, upon the folds of bandages,—everywhere where there is infectious matter, its qualities are incontestable. This is also true as regards putrid or gangrenous foci, fetid suppurations, sanious wounds, ichorous putrilagenous cavities, hospital gangrene, &c.; but upon acute and exposed wounds, or upon ordinary wounds or ulcers, other topical applications are preferable to it.

III. Used with lint upon cloths, with pomades or cerate, it has afforded no useful result, and nothing has occurred to prove that when administered internally it has produced the least benefit.

IV. As an absorbent it leaves much to be desired, although it is not entirely devoid of action. When applied as a poultice, in particular, it absorbs very incompletely. For that matter the mixtures of coal-tar with earth or with other powders, absorb still less than the mixture of Corne and Demeaux, and are scarcely at all applicable in therapeutics. In this connection it must not be forgotten that the morbid liquids, and particularly pus, are very different from water. A substance like plaster, for example, which absorbs water strongly, might be incapable of absorbing pus. It is nevertheless true, that as an absorbent, the mixture of coal-

tar and plaster, either as powder or as poultice, is of some use upon fetid and putrid wounds or suppurations.

V. Cellulose, glycerine and cherry-laurel water; chlorate of potash mixed with talc, clay, marl or kaolin, are neither sufficiently efficacious, nor in application are they convenient enough to be retained in practice.

VI. The mixture of saponine and coal-tar does not appear to be preferable for dressing wounds to many other liquids already known,—tincture of aloes for example. The same may be said of the mixed coal-tar and charcoal of Herpin; nor does it seem as if carbonic acid should be used, unless some improved method of applying it can be devised.

VII. The Boghead residue would be useful only in lack of coal-tar and plaster. While charcoal in porous envelopes does not mould itself to cavernous and sinuous wounds with sufficient readiness to come into general practice.

VIII. From its low price, and by its action, at once mild, absorbent, and disinfectant, as well as by its drying properties, the subnitrate of bismuth will render important services in default of the mixture of coal-tar and plaster. It is even preferable to this when the wounds are accompanied or surrounded with heat or irritation.

IX. Tincture of iodine and perchlorid of iron act rather by modifying the surfaces of wounds and of purulent foci, than as absorbents or disinfectants. They have their special applications in surgery, but agents of this sort are not comparable with the mixed coal-tar and plaster.

X. Sponges soaked in chlorinated water can also render good service upon pale, burrowing sores and upon gangrenous foci.

We have occupied ourselves, say the committee, only with the practical or experimental side of the question. A discussion of its theoretical or chemical bearings would have carried us too far. Moreover, since the authors of the different communications which have been submitted to us have themselves neglected this for the most part, it has seemed to us useless to treat of it at present; whether it be the phenic acid or rosolic, or brunolic acid, or the anilin, picolin, etc., of the coal-tar, which disinfects, is in reality of but little importance. Science will inform us of this some day no doubt; for the moment we have merely to ascertain whether or no the various disinfectants which are brought to us do really disinfect.

After citing the labors of various persons who have proposed methods of disinfection, the committee go on to say: "M. Corne, and the authors indicated above, occupied themselves only with the disinfection and the solidification of animal matter, having in view the preparation of manures. * * * * It is M. Demeaux who appears first to have had the thought of applying to fetid wounds, in surgical practice, the powder invented, or adopted and extolled, by his neighbor. In addition, it is evident that here, as is the case with so many other complex facts with which science is enriched, there is, so to say, neither invention nor priority for any one. The subject has been worked upon for more than a century—a multitude of savans having competed with each other in studying it. Little by little the evolution of the discovery has been effected. M. Corne disengaged it from its gangue a little better than his predecessors, and Demeaux, knowing, perhaps, that from time immemorial sailors and the inhabitants of certain southern countries often dress their wounds

with tar; that tar water and pomades of tar are frequently employed in medicine, has extended its applications to therapeutics."

"Many other efforts are still necessary. In point of fact the results thus far obtained are merely rough outlines,—only first trials. So long as the world at large is not in possession of a simple, easy, and economical method, accessible to every one, which shall be capable of disinfecting immediately, and without inconvenience on the large or small scale, dejections and filth of all kinds, in dwellings as well as in privies or slaughter-houses; in dissecting-rooms and the like, as well as in the sick room, upon wounds, improvements will still be wanted; there will yet be room for new attempts. While recording those of to-day and those of yesterday upon the road already traversed, let us be careful not to diminish the ardor of the laborers in the future, who will finally endow civilization with a complete and general disinfection."

Finally, certain indispensable precautions must be followed, in order to obtain from the process of Corne and Demeaux its proper effect. It is evident, from having neglected some of these precautions, that different experimenters have been led to believe that the method is useless. Fine moulding plaster, and not the common article, should be employed. The coal-tar, which is mixed with it in the proportion of 2 to 4 parts to a hundred, by triturating or grinding, ought to impart to it a gray tint, without destroying its dry, pulverulent condition. Objects to be disinfected should be rolled in this powder until each point upon their surfaces has been brought in contact with it. Gangrenous or putrid sores should be covered with thick layers of it, by handfuls, several times per day. If one is treating pus, blood, dejections, or the like, enough of the powder should be added to form a paste of the mass, taking care to replace the first layer of powder by another as soon as it no longer absorbs any more. Mixed with oil to the consistence of a thick pap, it forms poultices of convenient application, if they are made thick and broad.

Within the limits which have been indicated the mixture of coal-tar and plaster is a good disinfectant, and may be recommended for use in domestic economy as well as in hospitals. "What we have ourselves seen leaves no uncertainty of the reality of this property, nor of the possibility of its application." * * * * It remains only to draw from it reasonable, practical consequences, either taking the fact as it is, or by modifying and perfecting it.—*Comptes Rendus*, 1, 279.

[For corroborating testimony, received by the committee from various sources, the reader is referred to their report in question. Numerous other articles upon the subject, by different authors, may also be found in vol. xlix of the *Comptes Rendus*.—F. H. S.]

7. *Decoloration of Indigo by Sesquioxyd of Iron*.—[In the May number of this Journal we took occasion to maintain that the very interesting fact of the power of ferric salts to bleach solutions of indigo was first observed by Prof. H. Wurtz. Since then we have accidentally learned that this claim was erroneous, as will appear from the following statement made by Wöehler some twenty years since. "When a solution of indigo in sulphuric acid is mixed with salts of the sesquioxyd of iron and heated, it will be decolorized precisely as it would be by nitric acid."—(*Annalen der Chemie und Pharmacie*, 1840, xxxiv, 235; see also Gmelin's Handbook (Cavendish Soc. Edit.), xiii, 59.—F. H. S.]

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From John W. Graves
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REPORT

OF THE

JOINT SPECIAL COMMITTEE,

ON THE SUBJECT OF THE

EFFECTS OF LEAD PIPES

UPON WELL-WATER,

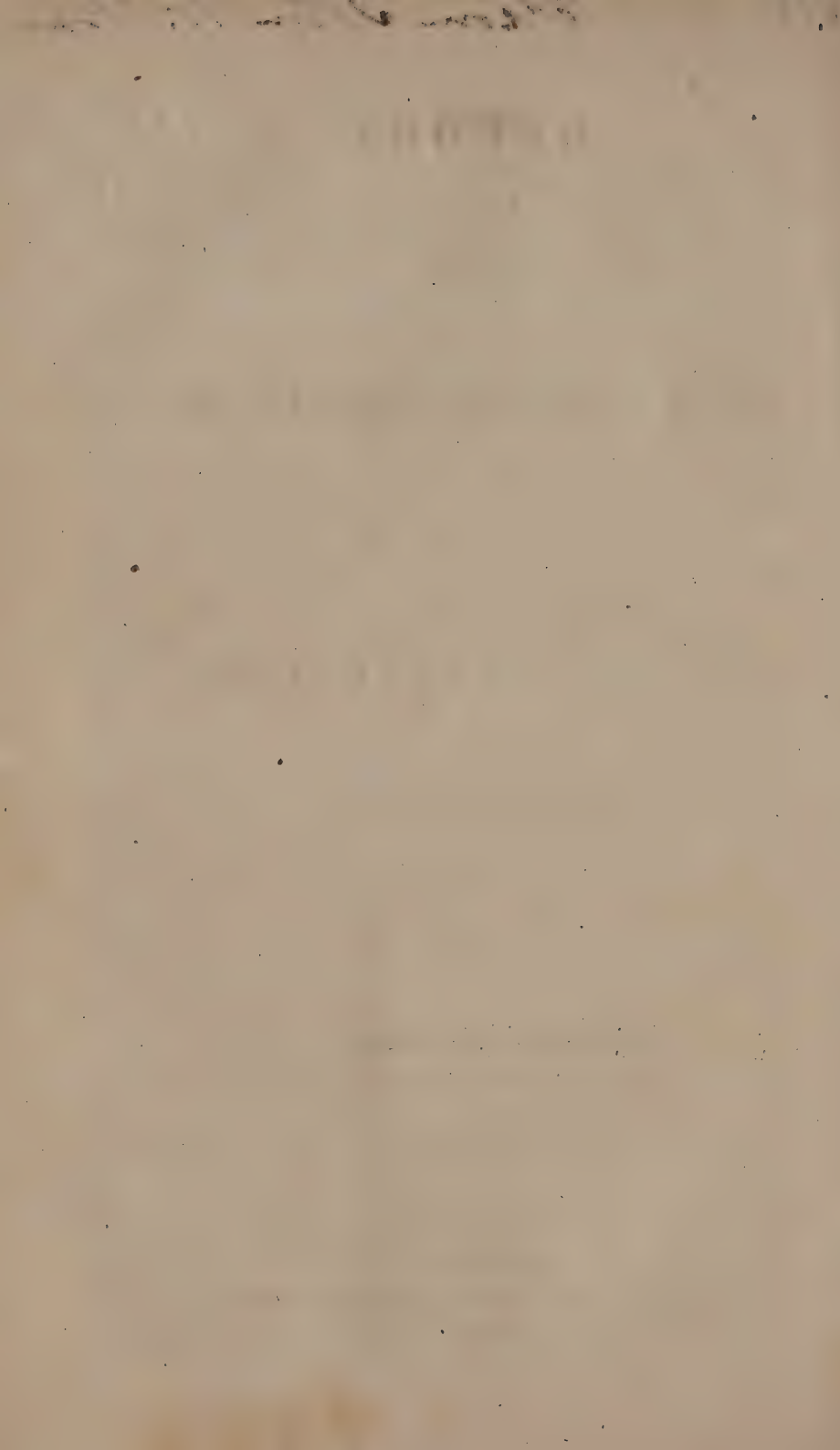
IN

THE CITY OF LOWELL.

LOWELL:

PRINTED BY WILLIAM SCHOULER.

1842.



*To the Hon. the Mayor, Aldermen, and Common Council
of the City of Lowell:—*

We, the undersigned, from facts which have come to our knowledge, have great reason to believe that many of the wells of our city are injuriously impregnated with *lead*, to the great detriment of the public health.

We deem it of great importance that the matter should be thoroughly investigated, and the results made public. We therefore pray your honorable Board to take such measures thereon, as, in your judgment, shall best promote the interests and health of a very large portion of our population.

Signed

ELISHA HUNTINGTON.

JOHN BUTTERFIELD.

DANIEL MOWE.

NATHAN ALLEN.

Lowell, August 1, 1842.

IN BOARD OF ALDERMEN, Aug. 1, 1842.

Read and referred to a joint special committee. Aldermen Graves and Beard appointed, to be joined. Sent down for concurrence.

THOMAS ORDWAY, City Clerk.

IN COMMON COUNCIL, Aug. 1, 1842.

Read and referred in concurrence, and Messrs. Jewett, Spaulding and Fitts joined.

GEORGE A. BUTTERFIELD, Clerk C. C. pro tem.

CITY OF LOWELL, AUGUST 15, 1842.

To the City Council:

The joint special committee to whom was referred the petition of Elisha Huntington and others, asking an investigation relative to the poisonous effects of leaden pipes upon the well-water of the city,

R E P O R T:

That having taken the subject matter into due consideration, and knowing that the water in wells into which leaden pipes are introduced is more or less impregnated with lead, consequently operating injuriously upon the health of those using such water, they regarded it a question of such importance as to demand a thorough examination. The committee in the discharge of their duty, procured the assistance of Dr. Samuel L. Dana, of this city, one of the ablest chemists in the country, and have received from him the accompanying elaborate communication, which is so full and satisfactory, that it is unnecessary for them to add any remarks or suggestions of their own, further than to commend its careful perusal to all who are interested in the subject.

The committee, for themselves and in behalf of the citizens, are greatly indebted to Dr. Dana, for the very valuable services which he has rendered in the investigation, and recommend that one thousand copies of this report and his communication be printed for the City Government and distribution. All of which is respectfully submitted.

JOHN W. GRAVES,	} Committee.
ITHAMAR A. BEARD,	
IRA SPALDING,	
ISAAC N. FITTS,	

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IN BOARD OF ALDERMEN, Aug. 15, 1842.

Read, accepted, and one thousand copies of the report and communication ordered to be printed. Sent down for concurrence.

THOMAS ORDWAY, City Clerk.

IN COMMON COUNCIL, Aug. 15, 1842.

Read, accepted, and ordered to be printed in concurrence.

JOHN G. LOCKE, Clerk Common Council.

*Correspondence of the Committee with Dr. Dana.**Lowell, August 4, 1842.*

SAMUEL L. DANA, M. D.

Dear Sir:—A communication relative to the poisonous effects of leaden pipes on the water of wells into which they are introduced, and the injurious consequences on persons using the same, has been made to the city government, and referred to a special joint committee. I am directed by this committee, to request you to furnish them with the result of your experiments upon the effects of leaden pipes on the water in the wells of this city. We also desire you to communicate to us, such facts, with your opinion, relative to the effects of water impregnated with lead, upon the health and constitution, with such other information on the subject generally, as you may deem important and interesting to be communicated to the public.

A compliance with the request of the committee, will, from your deservedly high reputation, afford them, as well as our fellow-citizens, perfect satisfaction on the above subject.

Very Respectfully,

Your ob't serv't,

JOHN W. GRAVES.

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*Lowell, August 9, 1842.*

SIR:—

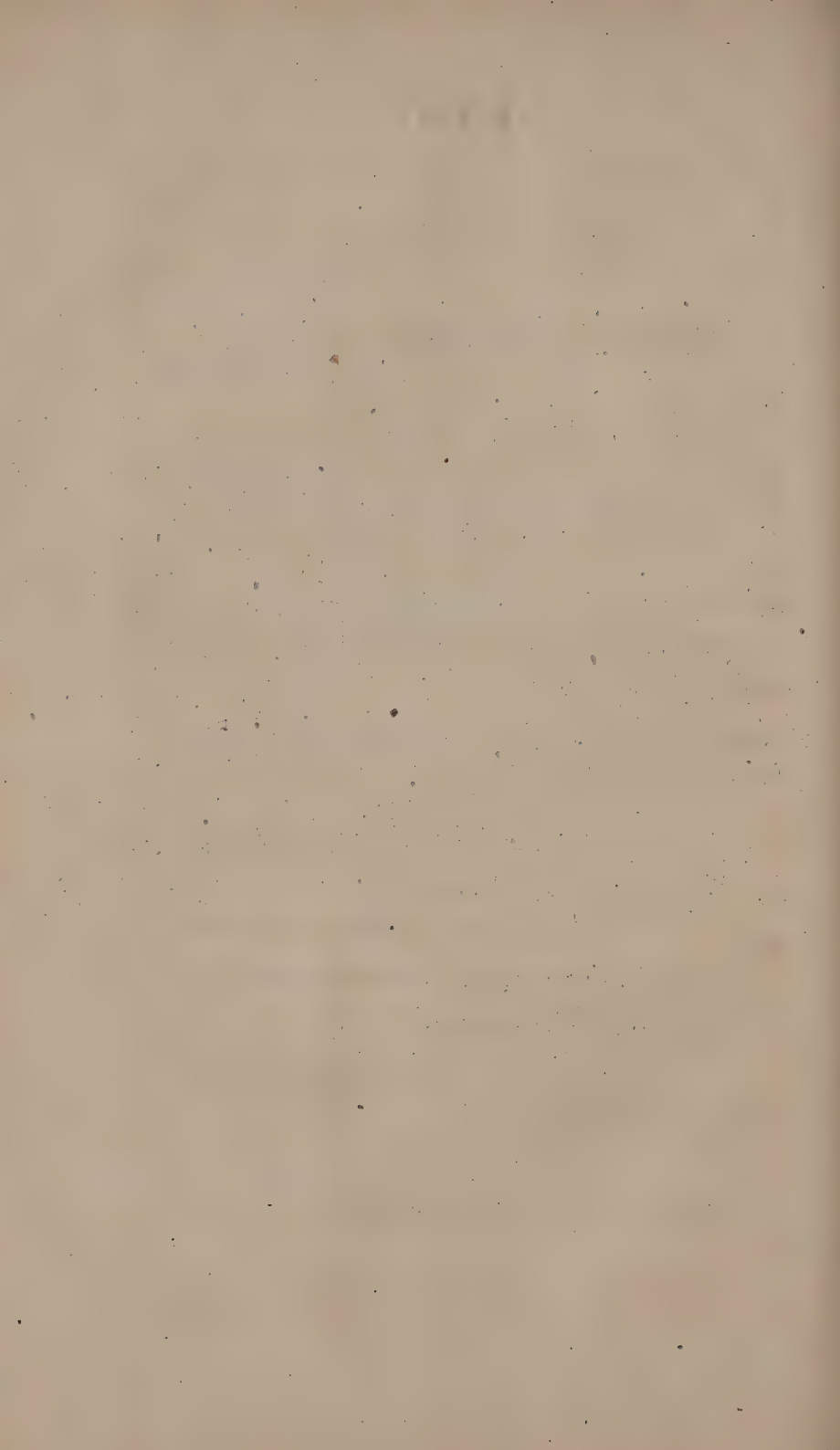
The following remarks, in reply to your letter of the 4th instant, are submitted, respectfully, by the

Committee's

Ob't servant,

SAMUEL L. DANA.

To John W. Graves, M. D. }  
Chairman of Committee. }





## OF THE MUTUAL ACTION OF LEAD AND WELL-WATER.

1. The true answer, to the first part of your letter, is to be found in the knowledge of the action of water, and of salts, upon lead.

2. Lead, scraped bright, and exposed to air, or water, soon tarnishes. This tarnish is the rust or oxide of lead. It forms fast when lead is heated in air, and still faster on melted lead. This rust, or dross, or oxide of lead, is dissolved by pure water, by alkalies, as potash, soda, ammonia, by lime. It is readily dissolved by various acids, particularly by nitric and acetic acid, or aqua fortis and vinegar, and by several vegetable acids. It rapidly forms in contact with fermenting matter, and is dissolved by the acid thus formed.

3. Pure water alone, will dissolve the rust of lead. One pint dissolves a grain of lead. Hence, the purer the water, the greater the amount dissolved.

4. The action of pure water is modified by the presence of carbonic acid. No natural water is pure. All contains carbonic acid. If the carbonic acid alone existed in water, that would change the dissolved lead into white lead, which would thus be diffused through the water, in small and invisible particles, requiring long repose to settle.

5. The presence of salts, also modifies the action of pure water.

6. The salts in the natural water of Lowell, are common salt, copperas, alum, saltpetre, salts of lime, such as sulphate

of lime or plaster of Paris, muriate of lime, and nitrate of lime, or saltpetre lime. It is a variety of saltpetre having the same acid as that, but its potash, replaced by lime. There are also small quantities of salts of magnesia, and of ammonia. The most abundant salts, are copperas, alum, the varieties of saltpetre, and common salt.

7. If the salts only modified the action of water upon lead, or if one salt alone existed, which soon of itself acted as a protector, which is the current opinion, then the presence of a salt would be a positive benefit ; for 1-2000 parts of Plaster of Paris would prevent the action of water. The salts themselves exist not single in water, but mingled. They act on each other, giving rise to products which act on, and dissolve lead. They act in some classes, themselves on lead, and the substance so produced, is dissolved by well-water.

8. The action of salts contained in Lowell water, though somewhat complicated, is easily understood. The most active among the salts, are those which have been said (section 6.) to be most abundant. These are copperas, common salt, and the variety of saltpetre called lime saltpetre. To understand how these act, let their composition be briefly stated.

1st. Copperas. It is composed of oil of vitriol and of iron. Exposure to air, rusts the iron, and a portion of the acid becomes free.

2d. The lime saltpetre is composed of lime and of aqua-fortis. The other varieties, of potash, or ammonia, or soda, and aqua fortis. The effect of mingling the free acid of the copperas, with these, would be, to set free their aqua fortis, which would then immediately dissolve the lead. Copperas alone, would act on the lime saltpetre, but in this case, no free aqua fortis is formed. The compound of iron and aqua fortis, now formed, is liable still to act on lead.

3d. Common salt is composed of soda, and chlorine ; muriate of lime, of lime, and chlorine. The effect of free acid of copperas is, to let loose the chlorine, or to form muriatic acid. This acts to dissolve lead.

9. The action of common salt, or muriate of lime, does not

depend upon free acid of copperas. Lead decomposes common salt. It unites with its chlorine, and thus forms chloride or muriate of lead, which, if heated, would be King's, or patent yellow. This compound, thus formed, as also that produced by the action of free muriatic acid, is easily soluble to a small extent in water, more soluble in acid water, and quite soluble in alkali. When lead then decomposes common salt, the soda, if no free acid is present, renders this compound more soluble.

10. From the variety of salts present in water, the soda produced as above, (9) is usually converted into sulphate of soda; or if muriate of lime, is decomposed by lead, there is also usually formed, in like manner, sulphate of lime. If free nitric acid, formed as stated, (8, 2d) is present, we have only formed the varieties of saltpetre.

11. When lead is dissolved in salt and water, the process continues till the salt is all used. After some time standing, the lead is re-deposited, in little distant, white knobs and threads, varying from the size of a pin's head to that of a pea. If these are removed, the lead is found to be pitted, and very bright in these places.

12. The facts to be chiefly remembered in (9, 10, 11,) are, that common salt corrodes lead—that the substance so formed is soluble in water—that it is still more soluble in nitric acid, whose presence in water has been shown possible, and in free vegetable acid.

13. That a large amount of such acid exists in Lowell waters; has been found by repeated analysis. This acid exists also in the rivers which flow through the city, and it rapidly corrodes, and dissolves not only lead itself, but also particularly the white substance produced by common salt and lead.

14. All alkalies, as potash, and soda, and lime, dissolve the compound of lead and salt. They decompose and dissolve the compounds of lead and oil of vitriol, or that formed by the action of copperas.

15. Were the salts of limited amount, it is evident that they would soon, in contact with lead, destroy their own action.



But their supply is as unlimited, as that of the water. Their origin may be here referred to. Those only, whose effects on lead are greatest, need here be regarded.

1st. Copperas. It arises from the natural decay of Iron Pyrites, or a compound of sulphur and iron.

2d. Saltpetre is well known to be constantly formed on the surface of the earth, wherever animals or vegetables decay. These form the acid, and the soil affords the lime and alkali. I have, in no one instance, and my analyses have been extensive, found nitrates or the various forms of saltpetre, absent from the well-water of Lowell. I have detected nitrates in several small streams in the neighborhood of this city, and once in the Merrimack. Probably nitrates will be found always in it during a freshet.

3d. Common salt. It comes down with every rain. I find this to have been the case in every fall since March last. It is probably a universal ingredient in rain water. Salts of lime, as muriate, perhaps sulphate, and of ammonia, also accompany rain. It is evident then, that the supply of salts is as exhaustless as the rain itself. Small in quantity to be sure, yet bountifully and beneficently supplied for natural operations, especially vegetation, and injurious only when man subjects his contrivances to those laws which regulate the action of salts on other matter.

16. The great and efficient cause of the action of these on lead, will be found in the natural decomposition of copperas, whose free acid then acts on the nitrates and muriates of lime.

The next most powerful corroder is common salt. The vegetable acid acts least in ordinary cases; though occasionally, I have found it so abundant in the Merrimack river, as to dissolve in twenty-four hours, as much lead as would pure water.

This explanation of the cause of the corrosion of lead, will be seen at once, by those conversant with the usual chemical books of the day, is counter to the current opinion. It would be offered with greater diffidence, were it not supported by two facts.

1st. Leaden pipes are extensively corroded, and in some cases, rendered thereby useless, in the well-water of Lowell. This fact is well known to many of our citizens. It is not confined to particular portions of the city, and occurs even in hard waters.

2d. Analysis detects lead in the water of Lowell wells, into which lead pipe is introduced. The analyses of the water of a great many wells, in different sections of the city, in no one of which, has lead been absent, authorises the conclusion, *that lead is dissolved by all well-water of the city.*

17. Lead may exist also in suspension in water (4). If the action of salts is, as has been supposed, to form a protecting coat over the lead, then, the tremulous motion communicated throughout the pipe by the act of pumping and other causes, would detach this first formed coat. It may be added, that lead, in such invisibly diffused particles, has been thought by many, to be the only form in which it is usually found in water, flowing through lead pipes.

18. Whether lead exists in water, suspended, or dissolved, is of little moment. The fact that it does exist, is of the highest interest. Nor is it of essential consequence to state the quantity per gallon which may be found. The quantity varies, dependent on two causes.

1st. Proximity to sources of nitrates and muriates.

2d. The geological character of the underlaying, and surrounding rock.

19. The sources of nitrates, are stables, styes, and vaults. It is not to be concealed, but deeply lamented, that the abomination of desolation standeth too often where it ought not. There is good reason for the opinion, that the common receptacle for the water which has been drank, is too near the source from which it was drawn, not to have affected its quality. In the wonderful laboratory of a vault, beautiful changes are going on which excite our admiration. The products of these transformations are harmless in themselves. They no longer remind one of their origin. Acting on metals, in obedience to laws, which were impressed on them at creation, we

cannot doubt but that the greater their production, the greater the chance that leaden pipes will there be most acted upon.

20. The geological character of particular districts of the city, affects the quantity of lead dissolved by the well-water. For popular use, Lowell may be naturally divided into three geological districts; each distinct, and which may be termed, 1st, the copperas; 2d, the gravel; and 3d, the clay district.

1st. Lowell reposes chiefly on slate rocks, of those varieties called mica, and talcose, or clay slate. The high ridge called Chapel Hill, extending from Concord river to the Railroad, and the ridge extending from the Railroad gap to the foot of Appleton street, are composed of mica and talcose slates, highly charged with sulphur and iron. This forms copperas (8). The water obtained from this ledge is charged with copperas. There are however, many places in this district, where the water is merely top water, which filters through the bed of covering gravel, down to the ledge, without entering it, and it is as free from iron as that obtained elsewhere.

2d. The remainder of Lowell proper, reposes on a more compact variety of slate, passing into clay slate, much less charged with sulphur and iron, and covered generally many feet in depth, with sand and gravel. The water in this gravel district is chiefly top water, which filters through the gravel, down to the rock; but even in the gravel region, veins of water are occasionally met, charged with the like salts, which are formed in that of the copperas district.

3d. That portion of the city, called Belvidere, reposes on clay, which again is underlayed by a rock, called gneiss. The clay is covered with a fine white, clayey gravel. The water of this clay district contains less copperas than that of the others.

21. Referring to these natural geological districts, and to the proximity to sources of nitrates and muriates, it is evident, that particular situations, and on these particular spots, will be found where lead will be much more corroded than on others. Hence, it is found by analysis, that some well-water is so highly charged with lead, as to be detected in a few minutes, by



the simplest tests, while others require an elaborate analysis, and delicate tact, to enable one to perceive that in them, lead exists. No case has come under my observation, in which lead has been absent. It may be stated as a general inference, that lead in water will be in proportion to the copperas, and muriate, and nitrate of lime. If the copperas was entirely withdrawn, the action of the muriates of lime and soda would be the next most active cause of the erosion of lead. The action of these last is much promoted by vegetable matter, in fermentation, or the natural decay of wood. Lead is sometimes corroded, only where in contact with decaying wood.

#### OF THE EFFECTS OF USING LEAD WATER.

22. The fact so well known to our citizens, that leaden pipes are corroded and destroyed by well-water, would long ago have told them the effects of using such water, were it not that the disorders produced by it are of such slow and insidious character, that they have been attributed to other sources, till chemical analysis has pointed out a cause of disease more to be relied on than doubtful speculation.

23. That lead, in continued small doses, is a cause of disease and death, is the accumulated testimony of two thousand years. Yet the metal is used where its use is most dangerous. Men are roused to a sense of its danger, only when the frequency of the disease, attended often by a fatal termination, has spoken in tones which chill the hearts of the bereaved, and alarm the living sufferers by well grounded fears, that the seeds of deathly disease may be germinating in their constitutions.

24. This is not the place, nor am I the person to enter into a detailed account of the symptoms of disease usually attributed to lead. Perhaps the time has not yet arrived, from want of accurate observation, to write even a brief history of such diseases. It may however, be stated, that the usual form under which we are accustomed to see the effects of lead, viz :—“Painter’s colic,” is only one form of its effects. Paralysis

too, constipation, dry belly achè, purging and vomiting are not unfrequently witnessed, consequent to the use of lead. These cases cannot, and generally have not been mistaken. But there is reason to believe that a vast many cases of rheumatic and spasmodic and nervous disease, a general breaking up as it were of the foundations of the great deep of life, have occurred, which can be attributed only to the effects of small, daily doses of lead. This disease, with general similarity of symptoms has sometimes pervaded whole families, and with a fatality, second only to cholera. Out of nine persons, four died ; the others were saved by removing from the cause. It produced death in from twenty-four hours after the attack, to four months. In none of these, were the slightest marks of disease visible on dissection. Nor was paralysis an accompanying evil.

25. Medical books contain records enough of the effects of lead, to warrant the conclusion, that it is a frequent cause of disease and death. That its use is not always, in all persons, followed by evil, is to be found in the fact, that every one has his own constitution, as he has his own face. The countenance, may not be so ill-favored as to forbid the hope, that possibly it may be, by some one thought handsome ; so too, in each man's constitution, it is only a presumption, that lead may not affect it. If we consider the chemical action of lead on the tissues of the body, it will be seen that the presumption is, that lead will, and does affect all constitutions. As it is not in the capacity of a physician, but of a chemist, that your committee have requested my opinion, I beg leave to confine my remarks on the effects of lead, to its chemical action.

26. What is the constitution, upon whose firmness we repose our trust, that lead is harmless? The constitution is only a greater or less degree, of vital force. Life is the vital force, manifested under the control of a higher influence ; the nervous influence it may be, too spiritual for the cognizance of our senses. The vital force is cognizable by its effects, as are the effects of electricity, magnetism, light, heat. The vital force is as much a power or agent, as is either of these. All agents

act chemically on the tissues of the animal body living, as they would upon dead matter: Their agency is limited, and controlled by the vital force. If that is strong, so much less is their action. One man differs from another, as a horse, for instance, differs from a man. A horse may take daily, for weeks, several grains of arsenic, without other effect, than a softer and more silky skin. In this sense of the constitution, a difference in degree only, of that agent called the vital force, it is found by experience, that the young, the delicate, soonest succumb, under the effects of lead drank in their daily drink, and like the dews of heaven, descending on all, the gentlest and fairest, first feel the chill, which soon closes in death.

27. Understood then in this sense, the vital force is continually opposing the chemical action of agents on the body. Lead belongs to that class of agents called poisons, the inorganic or mineral poisons. This class is distinguished from others, by this circumstance, that owing to the great tendency to unite chemically with the tissues of the body, they rarely pass into the circulation. These poisons unite with, and form a part of the living structure. The effect of this combination is, the total destruction in the part where it takes place, of the power of effecting and producing those chemical changes, in which mere life, unattended by nervous influence, consists; or in other words, poisons, by combining with the tissues, destroy their organic life.

28. A constant struggle is going on, between the vital force and the chemical action of the poison. If this is in small quantity, or of feeble power, or the vital force strong, then combination takes place only in a small degree. In some cases the poison remains combined, without producing the death of the part. In others, this destruction of the substance occurs, and is followed as a burn on the skin would be, by inflammation, and casting off the dead, by the living parts. In general, a great shrivelling of the parts to which the poison is applied, takes place. In other cases, the combination not totally destroying, but only impeding the healthy functions, goes on quietly for years, each year adding its force to the



preceding, yet leaving no visible trace in the parts, of its action, till finally the whole system becomes so combined with the poison, that death ensues. In the case of lead, the poison once combined with the tissue, is re-dissolved by an excess of the poison, and the parts are thus affected, with a general softening and pulpiness. This is, I believe, not an unfrequent trace of disease, which is found on dissection of those who have been supposed to have died from the effects of lead. From the chemical action of lead, it is evident, that we are not to look for marks of violent disease, after death, but rather for thickenings, hardenings, contractions, or great softness.

29. All mineral poisons act only when in solution, or are capable of being dissolved in the stomach. Arsenic, in its insoluble forms, is as harmless as sulphur. All substances which have the power of combining chemically with the animal tissues are poisons. But this class includes, especially, the metals, when formed into oxides or salts. Mercury, or corrosive sublimate, arsenic, lead, tin, zinc, copper. These all belong to the same class—they all operate alike—they differ only in the degree of force with which they operate. With this the constitution has nothing to do. Their difference in this respect is manifested as well on the dead as the living body. The same chemical combination takes place. In the living body, the poison, having overcome the vital force, that part is as much under the control of chemical laws, though surrounded by living parts, as if it were cut out of the body. Chemical combination takes place in definite proportion, and hence when it is considered that all the animal tissues, have, what chemistry calls, very high combining numbers, and the metals very low, it is easily seen how a very small proportion of the last may destroy a very large proportion of the first. About one grain of lead will completely neutralize and destroy vitality in one ounce of flesh or blood. How small a portion then, will impede the healthy functions of the body!

30. The mineral poisons then, all acting by uniform laws, the difference in their effects depends not upon constitution but upon their own inherent nature. This difference amounts

to this, that some operate at once like a hot iron, others only sear, without destroying the complete vitality of the part. They combine only slowly. This is the case, I suppose with lead. It is one of the poisons which from the smallness of its dose, and large dilution, I suppose enters the circulation. It gradually impedes the action of whatever part it combines with, bringing on disease, with a long train of anomalous symptoms, till finally, before the cause has been suspected, and while the sufferer is still under the daily influence of that cause, the deposited lead begins to be re-dissolved, a general softening of the vital organs takes place, and Death, the greater master chemist, closes the Laboratory of Life.

31. Who may presume then, considering the chemical action of lead on the human system, that his constitution is safe? Such presumption is indiscreet.

32. Those who have been unwittingly drinking daily, the seeds of disease, whose power is thus unfolded by chemical laws, I trust will not allow themselves to indulge in any unnecessary fears. It were much to be lamented, if the inquiry now set on foot, by our city, should result in alarm. If chemistry unfolds causes for fear, she also, angel like as she truly is, holds out greater cause for hope, to those who think themselves already under saturnine influence. Two remedies may be proposed, one acting wholly on chemical principles, the other on the principle of common sense. The last is, abstain at once from the use of lead water. The first is, drink daily for sometime, a small portion of sugared water, rendered sour as lemonade, by oil of vitriol. This will decompose the compound of lead, with the tissues, with which it may come in contact, and form a perfectly insoluble salt of lead which is harmless. Possibly, under this course, the poison may be finally eradicated from the system.

### OF THE SUBSTITUTES FOR LEAD WHICH HAVE BEEN PROPOSED.

33. The remedy (32) based on common sense, would lead to an abandonment of leaden pipes in our wells. The question is, what shall be substituted—cheap, efficacious, and wholesome. Here too, we must look to chemistry for the answer, if any metal except iron, is to be substituted for lead. Among the metals, copper, tin, zinc, or their alloys with each other, or with lead and iron, have been proposed. Let us first attend to the pure, that is, commercially pure metals themselves. Copper, tin, zinc, would each be, if used alone, acted on by the same salts and acids which have been shown (8) to act on lead. The compounds which they would form, are in each metal, much more soluble than the similar compounds with lead. The free sulphuric acid which may exist in water, not only in the absence of nitrates and muriates, would at once dissolve these metals, but the acids which would be eliminated from its action on such salts, will act with great energy on these substances. The same action which corrodes the copper sheathing of a vessel, will occur in well-water, on tin, zinc, copper.

34. It was shown (29) that the soluble salts of all these metals are poisons. Copper and tin are much more active than lead. Copper is easily reduced from a poisonous to a harmless state, by sugar. Tin more readily combines than lead, with the elements of food. Hence, though copper and tin are more active poisons than lead, they are less liable so to act. Zinc is least active. Indeed, it has been questioned, whether it acts at all as poison. From the laws of the action which have been stated, of these substances on the animal tissues, it may not be doubted that the repeated commissioners, authorized by the French Government, to investigate the effects of zinc, acted wisely when they uniformly reported against the use of zinc, in vessels used for private or public convenience.



35. From the earliest days, alloys of these metals have been used. Experience taught, that these alloys were less acted on than the separate metals. If water was as pure as air, then the same results might be anticipated from their use, as water pipes. But experience has also taught, that a portion of these alloys are, when in contact with certain substances, more rapidly acted on, than would be the separate metals.

36. These facts have remained unexplained till the days of Davy, and his explanation of the cause led him to protect copper by iron and zinc; and this again, has led to the protection of lead by tin, and of iron by zinc, under the name of galvanized iron. Now, as all these alloys and protectors have been proposed to be used, it may be not amiss to glance at the principle on which their action depends.

37. Two metals, in contact, are found to be in different states of electricity. One is positive; the other, negative. This depends not on any inherent power of the metal itself, for a metal positive with one, may be negative to another. The fact to be regarded is, that the metal upon which chemical action readiest takes place, is always positive. Hence the two sides of a single plate of metal will exhibit different electricities, if one be plain and smooth, the other rough. In general, that metal which rusts easiest, is positive to the other. Now, taking these facts as the guide, metals have been arranged in the following order, each being positive to all below it, and negative to all above it.

Zinc,  
Iron,  
Lead,  
Tin,  
Copper.

Each metal protects all below it. But this, the common order in air, is modified by the nature of the fluid in which these alloys, or galvanized metals are placed; for,

38. The order in alkaline solutions, and in solutions of common acids and salts, is as follows:

| In alkaline solutions (as lime-water): | In acid solutions (as Lowell well-water): |
|----------------------------------------|-------------------------------------------|
| Zinc,                                  | Zinc,                                     |
| Tin,                                   | Tin,                                      |
| Lead,                                  | Iron,                                     |
| Copper,                                | Lead,                                     |
| Iron.                                  | Copper.                                   |

39. The principle on which protection depends, is of the highest practical importance. That principle is, that the protecting metal is itself always dissolved. The above three series show, that different effects will take place in different circumstances. But, regarding here the last series, the facts are in accordance with the long and patient series of observations made in France, that in alloys of lead and tin, as pewter and Britannia ware, the tin is first dissolved. So, too, that profound chemist, Dr. Thomson, found the tin in tea lead, of which it is about four per cent., was always first dissolved. I have by me specimens of the material used in the original experiments of Davy, to protect copper sheathing by cast iron. Every particle of the iron is removed. It has been dissolved by the sea-water, and only a light, spongy mass remains, like black lead. It is the earthy and organic part of the cast iron.

40. Bearing these facts in mind, it is to be noticed, that leaden pipes are themselves sometimes adulterated. This accident arises from the natural impurity of the lead, or from the fact, that in melting large masses of pure lead, the rust or oxide, often is combined with the pure metal. This would be first attacked in those places. Impurities may arise, if old lead, often used with its solder, is employed to be drawn into pipes. Hence it is seen why lead is eaten in pits and channels.

41. The facts stated would lead us to anticipate what would be the result of using any of the substitutes for lead, which have been proposed. Of these, copper, tinned with pure tin, is the least objectionable; tin and lead, considering the variations to which they are exposed, the most objectionable. There remains zinc and iron, or galvanized iron, which would seem

to recommend itself by its cheapness, as it can be afforded, made from the sheet, including the bends, &c., of cast zinc, about as low as lead.

42. However confident one may feel, of the results of the action of salts and the metals, I was unwilling to discourage the resort to galvanized iron without experiment.

1. I find, that the zinc is rapidly dissolved, in a very dilute solution of common salt in water, and may be found in the solution, or water as the muriate of zinc. This would be the action of the common salt in rain-water, and it is the source of the corrosion of zinc roofs.

2. Galvanized iron, introduced into a solution of copperas in water, very dilute, acts thus: I soon found iron rust rapidly falling on the galvanized pipe. In a short time, *all* the iron was precipitated from the water, and fell in a coat of rust, while its place in the water was supplied by zinc. In other words, copperas or green vitriol was exchanged for white vitriol.

3. Galvanized iron, in a mingled solution of salt, and of copperas, such as is found in several wells in Lowell, is rapidly destroyed—the water becomes charged with salts of zinc.

43. I should therefore recommend—

1. Wood, wherever it can be used ;
2. Cast iron, or wrought iron tubes ;
3. Copper, protected either by pure tin, or still better, perhaps, with pure zinc.

The use of all other metals, and alloys of these, in the present state of our knowledge and experience on these subjects, ought forthwith to be abandoned.



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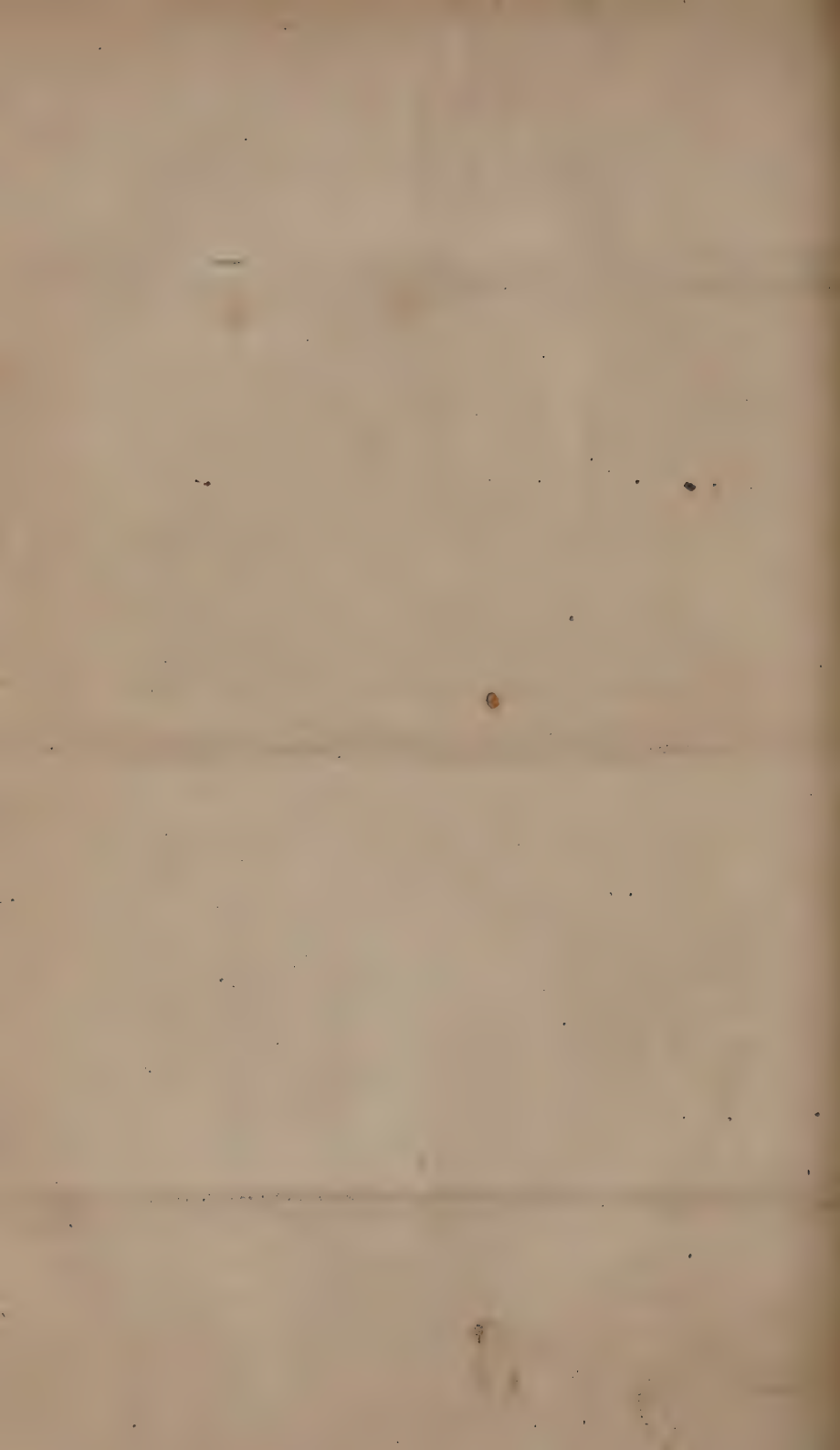
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## CURING AND PRESERVING BEEF AND PORK.

*Value of Solar evaporated salt as compared with the best foreign salts, determined.*

SEC. N. Y. STATE AG. SOC.:

DEAR SIR,—In the course of some investigations on the manufacture of common salt, I have had occasion to inquire into its uses, the adaptation of different kinds to particular purposes, and into some of the injurious effects which are alleged to come from the use of bad salt. Many of these being of a character to interest agriculturists, I have thought it might not be improper to present them to the notice of the State Agricultural Society.

One of the most important uses of salt is in preserving meat, butter, cheese, &c., and for this it seems indispensable. How it operates to produce this result and the precise changes which it effects in the substances preserved, are not fully understood. Liebig in his work on Agriculture and Physiology, p. 295, says, "salts of mineral acids with alkaline bases, completely arrest decay when added to decaying matter in sufficient quantity, and when their quantity is small, the process of decay is protracted and retarded." "Fresh flesh over which salt has been strewed, is found after twenty-four hours swimming in brine, although not a drop of water has been added; the water has been yielded by the muscular fiber itself, and having dissolved the salt in immediate contact with it, and thereby lost the power of penetrating animal substances, it has on this account separated from the flesh. The water still retained by the flesh contains a proportionally small quantity of salt, having that degree of dilution at which a saline fluid is capable of penetrating animal substances."

"This property of animal tissues is taken advantage of in domestic economy, for the purpose of removing so much water from

the meat, that a sufficient quantity is not left to enable it to enter into putrefaction."

Liebig in his "Researches on the Chemistry of food and the motion of the juices in the animal body," in discussing the properties of the juice of flesh, soups, &c., at page 109 and onward, says "when 1lb. of lean beef, free of fat and separated from the bones, in the finely chopped state in which it is used for beef sausages or mince meats, is uniformly mixed with its own weight of cold water, slowly heated to boiling, and the liquid after boiling briskly for a minute or two, is strained through a towel from the coagulated albumen and the fibrine, now become hard and horny, we obtain an equal weight of the most aromatic soup, of such strength as cannot be obtained even by boiling for hours from a piece of flesh. When mixed with salt and the other usual additions, by which soup is usually seasoned, and tinged somewhat darker by means of roasted onions or burnt sugar, it forms the very best soup which can in any way be prepared from 1lb of flesh."

"The influence which the brown color of this soup, or color in general, exercises on the taste, in consequence of the ideas associated with color in the mind (ideas of strength, concentration, &c.) may be rendered quite evident by the following experiment. The soup colored brown by caramel is declared by all persons to have a much stronger taste than the same soup when not colored, and yet the caramel in point of fact, does not in any way actually heighten the taste."

"If we allow the flesh to boil for a long time with the water, or if we boil down the soup, it acquires spontaneously, when concentrated to a certain point, a brownish color and a delicate flavor of roast meat; if we evaporate it to dryness in the water bath, or if possible at a still lower temperature, we obtain a dark-brown, soft mass, of which half an ounce suffices to convert 1lb. of water, with the addition of a little salt, into a strong well flavored soup."

"The tablets of so-called portable soup, prepared in England and France, are not to be compared with the extract of flesh just mentioned; for these are not made from flesh, but consist of gel-

atine, more or less pure, only distinguished from bone gelatine by its higher price."

"From 32lbs. of lean beef, free from bones and fat (8lbs. dry meat and 24lbs. of water), there is obtained 1lb. of true extract of flesh, which, from its necessarily high price, can hardly become an article of commerce, but if the experience of military surgeons agrees with that of Parmentier, according to whom "the dried extract of flesh, as an article of provision in the train of a body of troops, supplies to severely wounded soldiers, a restorative, or roborant, which, with a little wine, immediately revives their strength, exhausted by great loss of blood, and enables them to bear the transportation to the nearest hospital,"\* it appears to me to be a matter of conscience to recommend to the attention of governments the proposal of Parmentier and of Proust.

"Now that the composition of the extract of flesh is somewhat more accurately known, it ought to be easy for every well informed apothecary to distinguish the genuine from the false. Of the true extract, nearly eighty per cent is soluble in alcohol of eighty-five per cent, while the ordinary tablets of portable soup rarely yield more than four or five per cent. The presence of kreatine and kreatinine, the latter of which is instantly detected by the addition of chloride of zinc, to the alcoholic solution, as well as the nature of the salts left on incineration, which consists chiefly of soluble phosphates, furnishes sufficient data for judging of the quality of the true extract of flesh."

"I consider this extract of flesh as not less valuable for the provisioning of ships and fortresses, in order to preserve the health of the crew or garrison, in those cases where fresh meat and vegetables are wanting, and the people are supported by salt meat."

"It is universally known, that in the salting of meat, the flesh is rubbed and sprinkled with dry salt, and that where the salt, and meat are in contact, a brine is formed amounting in bulk to one-third of the fluid contained in the raw flesh."

\* See Proust, *Annales de Chimie et de Physique*, third series, Vol. 18. p. 177.



"I have ascertained that this brine contains the chief constituents of a concentrated soup or infusion of meat, and that, therefore, in the process of salting, the composition of the flesh is changed, and this, too, in a much greater degree than occurs in boiling. In boiling, the highly nutritious albumen remains in the coagulated state in the mass of flesh, but in salting, the albumen is separated from the flesh; for when the brine from salted meat is heated to boiling, a large quantity of albumen separates as a coagulum. This brine has an acid reaction, and gives with ammonia a copious precipitate of the double phosphate of ammonia and magnesia. It contains also lactic acid, a large quantity of potash, and kreatine, which although I could not separate that body from the large excess of salt, may be safely concluded to be present, from the presence of kreatinine. The brine, when neutralized by lime, gives, after the salt has been crystallized out, a mother liquid, from which, after some time, when alcohol and chloride of zinc are added to it, the double chloride of zinc and kreatinine, so often mentioned in the former part of this work, is deposited."

"It is now easy to understand that in the salting of meat, when this is pushed so far as to produce the brine above mentioned, a number of substances are withdrawn from the flesh, which are essential to its constitution, and that it therefore loses in nutritive quality in proportion to this abstraction. If these substances be not supplied from other quarters, it is obvious that a part of the flesh is converted into an element of respiration certainly not conducive to good health. It is certain, moreover, that the health of a man cannot be permanently sustained by means of salted meat, if the quantity be not greatly increased, inasmuch as it cannot perfectly replace, by the substances it contains, those parts of the body which have been expelled in consequence of the change of matter, nor can it preserve in its normal state the fluid distributed in every part of the body, namely, the juices of the flesh. A change in the quality of the gastric juice, and consequently in that of the products of the digestive process, must be regarded as an inevitable result of the long continued use of salted meat; and if during digestion the substances necessary to the transformation of that species of food be taken from

other parts of the organism, these parts must lose their normal condition."

"In my experiments on the salting of meat, I used at first a species of salt which subsequently proved, on examination, to contain a considerable proportion of chloride of calcium and chloride of magnesium. I was induced to examine the salt, by observing the brine obtained from meat salted with it, contained only traces of phosphoric acid. The external aspect of the salted flesh sufficiently explained this unexpected fact; for it was covered as if with a white froth, consisting chiefly of phosphate of lime and phosphate of magnesia. The earthy salts of the sea salt had entered into mutual decomposition with the alkaline phosphates of the juice, producing phosphates of lime and magnesia, of which only very small quantities could be dissolved in the acid brine."

"In the use of a salt rich in lime and magnesia, there may thus be a cause which renders the meat salted with it less injurious to the system. For it is plain, that when, along with such meat vegetables are eaten which are rich in potash, (and this is the case with all esculent vegetables,) the conditions are present which determine the reproduction, during digestion, of the deficient alkaline phosphates. That these latter salts may actually be formed under such circumstances, is shown by the analysis of milk, a fluid rich in alkaline phosphate, compared with that of the fodder or food of graminivorous animals, which last contains no alkaline phosphates, but phosphates of lime and magnesia, along with salts of the alkalies, with other acids"

The work from which the above quotation is made, is one of great interest to all who study the subject of domestic economy and presents a clearer view of the subjects upon which it treats, than has before been given, although the distinguished author says that it is very incomplete, and can only be taken as an introduction to the vast field upon which it has entered.

As illustrative of some of the points in it, I may state a few of the facts brought out last year \* in the report of a committee of

\* The investigation commenced Feb. 23, and closed April 30th, 1852.

the British House of Commons, "appointed to inquire into the contracts, and the mode of making them, for the supply of meat provisions for the use of Her Majesty's Navy from the year 1845 to 1851, inclusive, and to the rejection of preserved meats; and into the causes which have led to the receiving into the government stores, and to the issuing for the use of Her Majesty's ships on foreign service, certain preserved meats, which have proved to be unfit for human food; and into the means by which an occurrence so prejudicial to the public service may most effectually be prevented."

In this examination Thos. T. Grant, Esq., comptroller of the victualling department of the Navy, testifies that a complaint was made in November, 1851, from a vessel on the West India station, "that the salt meat issued to the crew of Her Majesty's ship *Alarm*," invariably weighing considerably less than half its original weight after boiling, more particularly the beef, four-pound pieces of which seldom weigh more than from one pound two ounces to one pound and a quarter; one piece yesterday, with two bones in it, actually only weighing nine ounces, as noted in the log; I beg leave to state to you, that every care being taken not to boil the meat longer than is absolutely necessary, the surveying officers, the senior lieutenant and master, are of opinion that this enormous shrinkage is attributable to the old and inferior quality of the meat; the beef we are at present using is dated October 1847, and was received from Halifax victualling depot, on the 15th day of September, 1851; the pork was examined January 1850, and was received from the Jamaica victualling depot, on the 28th day of February, 1851, &c., &c., Mr. Grant states that this "must have been very old meat which had been left in the depot in Halifax Yard, and had been subject to a tropical climate for a considerable time, and we find that under those circumstances meat will lose at least one-half, and even more than that from being exposed to the climate, and being subject to the influence of the pickle. The earliest complaint, so far as I have been able to ascertain, that was made upon this subject, was in 1788, in that year there were several complaints made by the seamen of the different ships, of the shrinkage of the meat after boiling, and the Admiralty of the day directed that experiments should be made at the Deptford yard for the purpose of as-



certaining what the loss in the meat was at different times and at different ages; and I find from the report that was then made, that meat which was only cured a few days, lost a third in weight, and according to the time that it remained in pickle it lost in proportion. I have here a statement of different experiments which have been made for the purpose of ascertaining what the meat really did lose. According to the present regulations, whenever the meat loses one-half in boiling, the men are supplied with an additional half-pound. Now we find that that is subject to very great abuse; in the first place the object of the cook is to boil away the meat as much as possible, because he obtains a larger quantity of what is termed slush, for which he is paid, and in some ships he is paid a very large amount, sometimes as much as £125, and £150, for his slush. On the other hand the seaman if he finds the meat boils away to half a pound, claims the additional half pound, but in fact he does not take up this half-pound, he saves it, and is actually paid at the rate of 4d. a pound for it, and the result is, that during the last two years we find that we have paid the seamen upwards of £50,000 for their savings in salt meat alone.

I have also pamphlets which were published by Mr. Cooper, and by Messrs Donkin, Hall and Gamble, in which they state, that on careful experiments the loss of the meat is exactly that which bears out the various experiments that we have made. They say the first experiment was made on the 27th of May 1813, on a fifty-six pounds keg of captain's beef, which had been about a month in pickle, weighing 56 pounds, It was then boiled by steam and the bones were carefully separated. The meat was suffered to cool and it was then found to weigh 35 pounds, deficiency 21 pounds; being, viz: bones 5 pounds 6 ounces, waste in boiling 15 pounds 10 ounces, total 21 pounds; being about 40 per cent loss. The second experiment was made on the 24th of July, 1813, on a half barrel of prime mess' beef, weighing 100 pounds net; which was salted in October 1812. On weighing the same prior to cooking it was 103 pounds. It is presumed that this increase of 3 pounds, arose from the meat being saturated with the pickle. It was then boiled as in the foregoing experiment, the bones carefully separated, and the meat suffered to cool, it was then found to weigh 47 pounds 8 ounces, deficiency

52 pounds 8 ounces; being, namely, bones 9 pounds 10 ounces, waste in cooking, 42 pounds 14 ounces; total 52 pounds 8 ounces, being more than one-half loss, &c. &c.

To the question whether he attributed this deterioration to the admixture of other descriptions of meat with the British meats, he answered "No; I think from the experience the officers at the victualling yards have of foreign meat they would be quite alive to that; they subject the meat to the examination which I have described, and they also subject the meat to the test of boiling, which is a sure test, but which I must say causes the greatest discontent on the part of the contractors."

To the question whether salted meats supplied under foreign contracts have been equally good with those supplied under British contracts: he answers "I must say the meat supplied from Hamburgh in particular and the Prussian meat and some of the French meat is quite equal to any meat supplied in the United Kingdom. I have my doubts as to the general quality of the American meat; we have been rather unfortunate with our American meat; we find now that there are very different qualities of American meat, some of it may be considered inferior meat at least not as good as our meat, but some of it is certainly first rate quality"

"I may add we have obtained information from several of the large ship owners both at Liverpool and London, Green & Wigram and parties of that description, and they invariably state that the merchant seamen prefer the American meats to those of the United Kingdom; and I must say that our report from ships generally speaking, with reference to Hamburgh meats and Dantzic meats, and French meats, as far as they have come to office, give the preference to those as compared with the meat of the United Kingdom.

"The first foreign meat was introduced into the service in 1847."

"The Hamburgh pork and the Dantzic pork, is said to be better fed than the Irish; it is decidedly a better fed, and larger description of meat, and at the same time it does not boil away even

so much as the Irish meat ; that is the result of the meat now under delivery, we find that it actually does not boil away a third, which is the amount which we allow for the receipt of meat. This is the case with pork as well as beef. It is to be ascribed to its being thinner meat, and to its being better fed. The observation we have made is this, that the best looking American meat, that is to say, the finest grown and the fattest meat, loses most in boiling. It is impossible to see finer looking meat, than that meat as it comes out of the casks, but it will not stand the test of boiling ; I suppose on account of the large quantity of fat that is attached to it. We have reason to believe that a good deal of this meat, under certain brands, is fed upon acorns, which gives it that fat appearance, but it has not the solidity which our meat has."

Capt. A. Milne, R. N., one of the Lords of the Admiralty, testified that "the average boiling away of meat in the first year is generally about thirty-three per cent., and it goes on increasing the second year to above forty per cent., and in the third year it is generally more than one-half. Has been in the Navy thirty-three years. No more complaint of pork diminishing in boiling, since there has been free trade in provisions, than formerly. The pork is considered remarkably fine, and is looked upon as superior to what we had before. We have had American, and Dantzic, and Hambro' and Brittany pork." "There have been no complaints of the pork or beef of any of those countries."

James Selfe, Esq., testified that he was ship's husband for Mr. Green, and that he had the entire charge of victualling twenty-seven ships, and had been thus engaged for thirteen years. To the question, whether there were many complaints of the boiling away of salt meats, his answer was "yes, we find that the cooks boil the meat too much ; we give them the slush as a perquisite ; there is a great deal in the way of boiling meat ; we insist upon the cooks putting the meat into cold water, but if you don't watch them very narrowly, they will put it into hot water, which destroys the meat ; if you put the meat into cold water, it gets heated gradually, and the internal part becomes boiled to the same degree as the external part ; but if you put it into hot



water, the outside is boiled, and the inside remains badly cooked." "If the American meat was not attended to, it would boil away more than other meat, because there is more fat."

The shrinkage on the best meat is from 22 to 25 per cent.

"inferior" 35 "40"

"We purchase the best salt provisions that can be got in market, India beef and India pork, and latterly we have given our crews American beef, in preference to Irish or English; we find it much superior." "We have purchased American beef for five or six years; and latterly when American meat of such a quality as we purchase was not in market, we have sent Irish beef; but our people do not like it so well; they complain of it, in fact the Irish meat is not so good now as it was seven or eight years ago." "The Irish pork is superior to the American, for sea purposes."

Edward Ede, Esq., assistant storekeeper at the Deptford victualling yard, on his examination stated his opinion of the quality of British and foreign cured meat, that he "preferred Hamburg meat, up to the examinations of last year; we have not had any this year, but this year certainly the palm has been carried off by the American meat branded "Abburger." "This is beef, not pork; the best pork we receive is certainly the Hamburg pork and the Dantzic, especially the Crasemann's and Koofman's brand, Hamburg. The best Irish meat, and which is the nearest to the quality of the Hamburg meat, is cured at Limerick, by Oake, or Shaw and Duffield."

Memoranda of the late comptroller of the victualling, dated in 1846, were also handed in to this committee. The comptroller states that the Deptford officers reported that the "experimental American salt beef was equal to the Irish salt beef, &c., &c." He also says, "since the alteration of the tariff, American salt meat has become an article of great import into this country, but the pork shrinks so much in boiling as not to be held in estimation. Much of the beef, however, is of a quality not inferior to the best Irish cured meat. There is, at the same time, a much larger quantity imported that is deep colored and hard, and of a very inferior quality, so much so as not to be fit for use in the navy."

"Of the American beef imported into this country that from the Ohio, Arkansas, &c., which comes through New Orleans, is generally of inferior quality, while that from the States on the shores of the Atlantic is, on the contrary, of excellent quality, particularly that imported from Baltimore. The meat cured at the latter place is generally from store cattle, driven across the Alleghany mountains, and fattened in the rich pastures on the coast."

Another memoranda dated in 1847 says that "previous reports on the quality of American beef were so satisfactory, as to have induced the purchase of 2,000 tierces last year; and a report has been received from Commander Murray, of the 'Favorite,' stating 'that the American beef was superior to any that he had ever seen issued to a ship's company, and that it was of a fine quality, and lost very little in boiling.' No report has yet been received on the quality of the American pork purchased for experiment, except that it was considered, at Deptford, when received, to be of a superior quality."

The test by boiling is one much relied on at the victualling yard at Deptford. When there last summer, the Commandant, Capt. Dundas, allowed a copy of one of their reports of an examination of beef, to be made for me, and as it will give some idea of the manner in which the trial is made, I insert it here.

*Extract from the Deptford's officers' report, dated Deptford victualling yard, April 15, 1851 :*

"We have made three comparative trials of American and Irish cured beef, by boiling each until properly cooked, and the following are the results :

|                                    |                    | Raw. |    | Boiled. |    | Loss. |    |
|------------------------------------|--------------------|------|----|---------|----|-------|----|
|                                    |                    | lbs  | oz | lbs     | oz | lbs   | oz |
| No. 1, ribs boiled 2 hours, Irish, | Wood's Brand,      | 8    | 10 | 5       | 6  | 3     | 4  |
|                                    | American, Hough's, | 8    | 9  | 4       | 2  | 4     | 7  |
| " 2, sirloin, " 2 " Irish,         | Wood's,            | 8    | 11 | 6       | 4  | 2     | 7  |
|                                    | American, Hough's, | 8    | 10 | 4       | 8  | 4     | 2  |
| " 3, brisket, " 2 " Irish,         | Wood's,            | 8    | 7  | 6       | 3  | 2     | 4  |
|                                    | American,          | 8    | 4  | 4       | 12 | 3     | 8  |

In the above experiments, both sorts of meat were put into cold water when placed on the fire, and the water on reaching the boiling point, was kept in a simmering state until the meat was dressed. We do not think the American meat requires less time in cooking than the Irish, for on trying a piece of the former, weighing about eight pounds, with an hour and a half boiling, it was almost raw in the middle, and when properly cooked, it is harder and not so nice in flavor as the Irish.

“We repeat what we have already stated in our reports of the 27th ultimo, and 8th instant, that the appearance of the American meat in its raw state is excellent, and we have no doubt those who provide for the mercantile marine are pleased with the sight of the article. We would suggest it as being probable, that the cattle from which the meat in question was procured, had been after a severe winter, sent in a lean state into rich pasture, and consequently so rapidly fattened, as to prevent the proper consolidation of the muscular fiber and fat, so that the process of boiling reduces the weight by evaporation, more than the meat of cattle fed less rapidly.”

Edward Ede, Esq., assistant store keeper at Deptford, informed me that in the trials of beef in 1852, the Irish lost more than thirty per cent., the American twenty-eight or twenty-nine, and Hamburgh and English, twenty-five per cent.

The presence of chloride of calcium and chloride of magnesium in salt have generally been thought injurious; they give to salt a tendency to deliquesce or run in wet weather, and frequently give to it a sharper and more pungent taste. All unite in considering them an inconvenience, but it will be perceived that Liebig in the article quoted, looks upon them as decidedly beneficial, and in the Gardeners' Chronicle and Agricultural Gazette for Feb. 8, 1845, in a report of the Agricultural Chemistry Association, several points of general interest to agriculturists are mentioned as having been inquired into, both analytically and practically. The eighth of these is “practical farmers, in dairy districts, having remarked that certain varieties of salt most favored the storing of their cheese; this subject has been inquired into, and those varieties which contain most of the deli-



quescent chlorides, have been found to be those which in practice answer best. This is rather remarkable."

In the course of my inquiries, I have frequently found the most violent and groundless prejudices against particular varieties of common salt, existing in the minds of intelligent and practical men. The distinguished Dr. Samuel Mitchell, of New-York, in 1803, wrote a letter to Dr. Caldwell, on the injurious properties of Liverpool salt. This letter was published in the Medical Repository, vol. 7. He says, "In the course of trade between America and Great Britain, it has become the misfortune of the United States, to be visited with frequent cargoes of salt from Liverpool. This article is prepared on the western coast of England, where coal for fuel can be bought at a low price, by boiling ocean water or briny spring water, saturated with the rock-salt of Northwich, in large and shallow pans of iron. The native mineral salt of Cheshire, is carried coastwise to Lancashire for that purpose. The salt which remains after the water has been evaporated by force of fire, is called *pan salt*, and is a medley of saline substances. It is very different in its qualities from the pure muriate of soda; for whereas that is the most agreeable of the antiseptics, and ranks among the strongest; this mixture of impurity and trash is remarkable for possessing the reverse of those valuable properties. Indeed, this *artificial* salt is exceedingly unlike the salt formed by the evaporation and crystallization, which sea-water *naturally* undergoes in the warmer latitudes. There is a remarkable difference between that vile and heterogeneous mass sold in the American ports, under the name of *blown salt* or *Liverpool salt*, and the efficacious and excellent article brought from the Canaries, Cape de Verde and Bahama Islands.

"The frequent and intimate connexion between the American ports of New-York, Philadelphia, Baltimore, &c., and the town of Liverpool, has rendered it very convenient, in the course of commerce and navigation, to throw in salt at the latter place for ballast, or part of a cargo, to the American market. The cheapness of fuel from the neighboring coal mines in Lancashire, enables the salt boilers to sell their manufacture cheap; and hence it happens that ships about to come to America, either empty, or with

a light freight, find it worth their while, as they must have ballast, to buy salt for the purpose instead of stones, sand, iron, or the like. If the salt clears itself, after paying prime cost and duties, it will answer as well as other ballast. If it does more than this, it is preferable."

"From this concurrence of events, it has happened that the sea ports of the United States have been largely supplied with British home-made salts, from Liverpool. Almost two-fifths of all the foreign salt consumed in the United States comes from this part of England. And a material more pernicious in its consequences could hardly be introduced among our people. The importation still continues, and the time is come to apprise and warn them of the evil. It is highly to be wished that never a bushel more of that mischievous commodity should be consumed in America. The trade in it ought to be broken up. If the consumers of salt were aware of the bad quality of that from Liverpool, there would be little probability of their continuing to use it or of purchasing a bushel more.

"Liverpool salt is very imposing to the eye. It is in a fine powdery form, of a tempting color, and possesses all the exterior qualities which allure purchasers, and invite a ready sale. The manufacturers possess in an uncommon degree, the art of preparing their ware most handsomely for market.

"It has accordingly been bought with avidity, by the American merchants and traders, and transported to many into the interior parts of the United States. The snowy whiteness of the material itself, its ready solubility in water, and the mildness of the pickle which it forms, had brought Liverpool salt into general use for preserving the beef, pork, and butter, of the middle and southern States.

"The loss of property and of life consequent upon the use of this kind of salt, is prodigious. Experience year after year, has proved it to be incapable of preserving our beef from corruption. Often has this important article of food been found to be tainted, the very autumn in which it has been packed in barrels. More frequently has the beef stunk abominably in the magazines and warehouses of New-York and other cities, on the return of warm

weather the ensuing spring. And a more common and lamentable case is, that in the progress of summer's heat, aided by a southern latitude, the beef when exported to the West Indies or elsewhere, degenerates with a still more rapid process of putrefaction.

"The inspectors who repack our beef, the merchants who own it, and the masters of vessels who carry it abroad, are all witnesses of these facts.

"But the waste and destruction of property are not the worst consequences of trusting the preservation of beef to Liverpool salt. The exhalations from such masses of animal flesh, as they undergo corruption, and turn to rottenness, are remarkably noxious. They poison the surrounding air by their deleterious presence. They have sickened and destroyed repeatedly in New-York, the inhabitants, who were unfortunate enough to be in the neighborhood of such nuisances, and enveloped in their unwholesome atmosphere. Pestilence and desolation have prevailed in the vicinity of these putrifying remains of oxen, bulls and cows.

"The misery endured by cities is also incidental to ships, within the sides, and under the hatches of a vessel, septic vapors are copiously engendered, and most highly concentrated. Existing there in their greatest virulence, they excite fevers of the most fatal forms that afflict the human race, and thus, from the nature of their cargoes, can it be understood wherefore vessels that carry beef, &c., to the West Indies are commonly sickly, and by the time they get back, are in an odious and intolerable state of uncleanness. Too pestilential from the venom engendered within them, to be admitted to port, they are proper subjects of *alkaline purification*, by which alone can they be rendered sweet, safe, and wholesome.

"Thus, besides the sacrifice of property, we find that the employment of Liverpool salt, in pickling beef, leaves it liable to corrupt; and the consequences of this corruption are pestilential exhalations, stirring up yellow fevers, and other malignant distempers in the neighborhoods of cities and vessels, where the bodies of these herds of slaughtered meat cattle happen to be deposited. Indeed, the mischief accruing to housekeeping, to city police, and to navigation, from this source, almost exceeds enumeration.



“There is another evil, however, which ought to be mentioned; that is, the disorders of the stomach and intestines induced by eating semi-septic beef and pork. It is well known to each master of a house, as well as to every master of a ship, that sometimes their salted provisions become tainted or partially spoiled. The expediency or necessity of the case obliges the family or crew to subsist upon this unsound and unhealthy food. Dysenteries, fluxes, scurvies, and similar ailments, are the natural ailments to this kind of diet. Sometimes among the customers of a country storekeeper, the extent of the sales of his British salt can be traced in the region around, by the offensive and disgusting condition of their meat tubs, and the prevalence of bloody fluxes, and other intestinal disorders in those who draw their sustenance thence.

“The loss of property, health, and life, which results from the vitiated and corrupt state of our beef, whether consumed at home or exported to foreign parts, is likewise consequent upon the use of Liverpool salt, or other British boiled salt, to pickle our *pork*. But as pork, from its nature, is less prone to corrupt and emit venomous gases than beef is, and is brought in smaller quantity to market, there is proportionably less damage sustained from its putrefaction, and less injury from its exhalations. But pork as well as beef suffers all that it can suffer in deterioration, from the weak and adulterated material wherewith it is salted. And thus the vessels in the West India trade grow foul and sickly. Their crews contract yellow fevers from the causes existing within themselves, and then the blame is cast upon foreign dominions.

“The butter of the New-York market has also been rendered worse, if not absolutely spoiled, by the same kind of salt. Beguiled by its fine and showy exterior, the citizens have used it extensively in our counties, famous for grazing and dairies. In many cases it has supplanted the old fashioned coarse or sun made salt. Wherever this substitution has been made, it has been with a pernicious effect. The butter so salted does not keep so well, loses its agreeable flavor, and acquires rather a disagreeable scent. It is less prized by those who are nice in selecting this important article of housekeeping, and it consequently brings a lower price to the

person who makes it. Thus agricultural industry is deprived of a part of its reward, and this will probably continue until the buttermakers discontinue altogether this very unfit and unsafe material. The difference between butter put up with this salt, and with the natural chrystallized salt is so great, that our wholesale and retail grocers can distinguish it at once by the smell, on piercing or opening a firkin. The sweet flavor and nice odor which pure sea-salt gives, is altogether wanting in that which is seasoned with the other, &c., &c."

In a report made to the minister of agriculture and commerce, of France, in 1847, upon salt ponds, (*les marais salants*), and the manufacture of solar salt; it is stated that a favorable prejudice has long kept up the character of the salt made on the west coast of France. It was thought preferable to that made on the Mediterranean coast, about Marseilles, for salting fish. The latter was said to be too active, too corrosive. Now the results of a series of experiments made with great care, from 1827 to 1830, by order of the Minister of the Interior, by a commission composed of men of the most eminent scientific attainments, M. M. Thenard, Gay Lussac, Berthier, &c., show that in comparative experiments made with salt from Marseilles, from the Atlantic coast of France, and from St. Ubes, all succeeded equally well. They even remarked that codfish prepared with Marseilles salt, acquired new qualities with age, and kept better, and it appeared that the Americans, easier suited, or more knowing than the French, gave willingly the preference to Marseilles salt. They take advantage of the return of their vessels, to load them; and the strange sight is seen of French fishermen going to St. Ubes for their supplies of salt, while the Americans come to France for theirs. The only possible difference there can be between the two kinds, is that the Marseilles salt is most free from dirt, and foreign substances.

Last summer when at Dieuze, in the eastern part of France, where there is an extensive manufactory of salt, and where the salt is of an excellent quality, and very pure, I saw a large pile of blue clay, and on inquiring its use, was informed that it was

for making *grey salt*. By mixing this clay with the pure white salt, in the process of manufacture, they could produce an article demanded by some of their customers, who seemed to think the excellence and strength of salt depended on the darkness of its color.

The amount of provisions damaged, and spoiled every year is enormously large. I have no accurate statistics to show the amount with precision, but both packers and dealers unite in the statement, that the losses from these causes are very great. In the fall of the year, it not unfrequently happens that great quantities of meat becomes tainted after it is salted, and before the salt *strikes*, and beef in particular, even when not otherwise damaged, is darker colored for being packed in warm weather. Beef packed in casks made of green wood, is sometimes made quite black on its surface, from this cause. Pork packed in March or April, is very liable to rust. And it is not unusually the case, that with an over anxiety to preserve meat, persons add an extra quantity of salt, this of itself is a serious injury to it, and will give it a black color. But upon these various points, I am glad to be able to present the results of the experience of an inspector and packer of beef and pork, who has been engaged in the business for many years past, and who has coming under his observation annually, from 25,000 to 50,000 barrels. C. Seguire, Esq., No. 518 Washington Street, New-York, has very obligingly furnished to me answers to the following questions.

NEW-YORK, *Feb 15th 1853.*

MR. GEO. H. COOK,

*Dear sir*—Accompanying this I send you answers to your queries transmitted along with yours of the 19th ult., with which I also received the report named.

I have found it a matter of more difficulty than I had supposed, to find time to give the subject the attention that its importance demands, and am fearful that you will be much disappointed in the matter and manner of my replies. The qualities that go far to make a successful business man are not such as would qualify him to *generalize on paper*, in my own case I have felt it to a painful



degree, and I hope that in this case you will take the will for the deed, and be enabled to glean something from the papers that will assist you.

It is just twenty years ago since I entered this business, during which period I have inspected annually from twenty-five thousand to fifty thousand barrels of provisions, besides cutting, packing and curing many thousands of hogs. My time and attention has consequently been more taken up with the management of a large business than with the *chemistry of the pork trade*, but as a matter of course, observation has been forced upon me, and what are *facts* to me would be theory to others of little or no experience.

I beg you will use these notes or throw them aside as you think best. If I make any request at all it will be that in case you do use them you will put them in better shape.

My only hope is that I may be of some use to you or others. If it should prove so it will much gratify.

Yours respectfully,

C. SEGUINE.

*Question 1.* What is the method of salting and packing beef which you approve?

*Ans.* The most approved method of curing and packing beef is first to "strike" it in open vats or hogsheds, i. e. pack loosely and cover with a pickle only, the pickle to be as strong as possible, and to contain saltpetre in the proportion of three ounces to the one hundred pounds of beef. It is in this first process that the red or cherry color is given to beef, and if not done in the first instance, no after application of saltpetre will supply the deficiency of color. As the market value of the article is greatly influenced by its color, too much care cannot be exercised to obtain this desideratum in perfection, and the process indicated above is decidedly the best. A week or ten days in the vats is sufficient to draw out the blood and fix the color, when it is packed with about twenty-five pounds of salt to the hundred pounds of beef, and pickled with a strong new pickle. With proper care beef packed in this manner will keep for the longest voyages.

*Question 2.* Also of pork ?

*Ans.* Pack with a light quantity of salt say thirty pounds per barrel of two hundred pounds, and pickle with a strong pickle. No saltpeter is required for pork ; repack early in the spring with forty pounds of salt and a new strong pickle ; hams should be packed with from seven to fifteen pounds of salt ; the lesser quantity will make the finer ham ; pickle with a strong pickle, adding about a pint of molasses and six ounces of saltpeter for every hundred pounds of ham. All pork intended for smoking should have saltpeter applied to give the lean a lively cherry color ; as also pork packed for the English market, the use of saltpeter being general with the English packers on all descriptions of pork.

*Question 3.* Is there more difficulty in preserving one than the other ?

*Ans.* Beef is more readily cured than pork but is less tenacious of cure, or more liable to spoil by exposure to the heat of summer. That it cures the more rapidly of the two, is I think evident from the fact that it absorbs or dissolves salt with much greater rapidity. The comparatively open or spongy nature of beef, containing a large percentage of blood and watery juices, readily yields to the action of salt which is brought in contact with every particle of the beef. Pork from its more compact fiber absorbs or combines with salt more slowly.

*Question. 4.* What is the effect of putting too much salt on meat ?

*Ans.* By hardening or constricting the fiber, the juices of the meat are *expelled* instead of combining with the salt. The meat is thus left to the caustic action of the salt, and is rendered hard and colorless ( black ) possessing neither the flavor nor nutritive qualities of meats properly salted. Beef always loses in weight immediately after salting, but if a proper quantity only is used, it regains that loss and afterwards increases in weight by absorption, three or four per cent ; if over salted it will exhibit no increase. This is owing to its hardness causing enlargement of the *cells*, if I may use the expression, preventing the meat by capillary attrac-

tion from holding or retaining its juices. Beef properly salted retains its bulk, oversalted it becomes shrivelled. Pork oversalted will not gain so much in weight as if properly salted, i. e. it will not absorb and hold as much pickle.

*Question 5.* Why is saltpeter used and what is the effect of using too much?

*Ans.* Saltpeter is used to fix or give a natural cherry red color to the lean of meats, it has no visible effect on fat; too much imparts a fiery dark red color to beef, detrimental to its sale and injurious to its flavor.

A French chemist of celebrity asserts that its use in the cure of meats is the principal cause of scurvy in those with whom salt meats are a principal food, as sailors on long voyages. So I will leave this question to the chemist to whom it properly belongs, remarking that my observation has been drawn rather to the effect of saltpeter on the appearance of the article; appearances having more to do with its value as merchandise, than the intrinsic nutritive quality.

*Question 6.* Have you ever observed the rind of pork to be partially or wholly destroyed when a sufficiency of salt had been used?

*Question 7.* What is the cause of this? Is it peculiar to some kinds of salt?

*Ans.* The rind of pork as a general rule becomes softened by the action of pickle, it is one of the sure indications of the length of time the pork has been barrelled. I have seen the rind entirely decomposed or softened in pork packed with a sufficient quantity of salt, after being in barrel two years, but accounted for it on the ground that the pork was packed from very young hogs, such as are known as *spring pigs*, which would give an age of nine or ten months, and in which case there was an evident want of bone and fiber owing to the rapid and extreme fattening.

The want of sufficient salt and lying in weak pickle is in most all cases the cause of such decomposition, and pork in this condition is generally tainted.



I have not noticed any difference in the action of different salts in this respect.

*Question 8.* Have you ever observed beef to be blackened by the wood of casks?

*Ans.* Casks made of unseasoned wood containing much sap, I have noticed will give a dark color to beef lying in immediate contact against the wood but not extending further into the cask of meat.

*Question 9.* Have you ever observed it to take place from an excess of salt being used?

*Ans.* See answer to No. 4.

*Question 10.* Does the color of the beef depend upon the animal, ox, steer, cow, or heifer, or upon the age, condition, feeding &c.,?

*Ans.* The color of beef after salting is somewhat influenced by condition and feeding, but not to an extent to call for remark.

*Question 11.* Have you observed any ill effect from the use of fine salt in packing?

*Ans.* Understanding you as meaning *Onondaga* "fine salt," I answer that I have observed "ill effects" from its use. Beef packed with fine salt I have generally found hard and dark colored, with a whitish deposit on the surface having the appearance of lime. This latter effect is almost invariable and is rendered the more perceptible in the article of smoked beef which is always first subjected to soaking in fresh water to soften it and draw out surplus salt and afterwards hung up and smoked in the smoke house eight or ten days; when taken out, it presents a dry burnt appearance on the surface, a mixture of brown and white, on cutting it open it is found to be black and dry possessing little flavor or substance. Kanawha fine salt is liable to the same objections made to the *Onondaga* fine salt. It is now used principally for dry salting or "bulking" pork in the west. Taking the receipts of pork in New Orleans as a criterion, about one-sixth of the pork packed at the west is "cured in dry salt." Pork so treated is

generally of an inferior quality, and soon becomes "rusty" or rancid.

The Liverpool ground \* salt is equal to the best Turk's Island and none of the objections made to our domestic fine salt can be made to this. It is not used much for pickling purposes, but is largely employed in the curing of fine hams and bacon in the New-York market. The "fine\*" or "factory filled" or "blown" is not employed in the curing of meat to any extent.

Pork packed with fine salt after a few months is found to have become changed in its appearance, the fat is turned brown and the lean black, and this in so marked a degree as to be confounded with rusty pork. Rusty or rancid pork is produced by the article being exposed to the action of the dry summer's heat after the pickle has been lost from the barrel for some time.

*Question 12.* What effect has overheating animals just before slaughtering on the quality of the beef?

*Ans.* No very marked effect; it is rendered somewhat flabby and rather more difficult to cure.

*Question 13.* What effect has it on meat to pack it before the animal heat is out?

*Ans.* This is the principal cause of the tainting of beef after packing in tight casks, hence the advantage of the mode of curing or *striking* in open vats as recommended in my answer to your first inquiry. Pork the same.

*Question 14.* Have you observed differences in salt meats which could be attributed to the kind of salt used?

*Ans.* See answer to question 11.

*Question 15.* Is there any difference perceptible between pork or beef cured with the Onondaga solar evaporated salt and Turks' Island salt?

\* Liverpool ground salt is known in England as "common salt;" it is coarser than boiled salt, and is made in brine not boiling hot. The "fine" or "factory filled" is boiled salt and is known in the English market as "stoved" or "butter salt."

*Ans.* There is no difference perceptible in either beef or pork, o packed and cured.

The best beef received in New-York is packed at Chicago, Illinois, where they pack each season beginning early in October and extending to the last of November, from twenty thousand (20,000) to twenty-five thousand (25,000) head of cattle, nearly all of which is cured and packed with *Onondaga solar evaporated salt*. In some few instances Turk's Island salt has been procured and used, but with little or no perceptible advantage over the other kind. The packing of pork at the same point amounts annually to about 25,000 hogs, all of which is cured and packed with *Onondaga solar salt* and for cure and appearance is second to no other pork packed in the country. These facts are satisfactory to my mind that for curing and packing beef and pork, the solar evaporated Onondaga salt is equal to Turk's Island salt. It is equally soluble and about the same gravity. In the latter respect it is only excelled by the St. Martins, Anguilla and Bonaire, which from their superior coarseness and hardness are preferred for repacking beef intended for long voyages.

*Question 16.* Have you observed that beef which has been salted two or three years loses more weight in boiling than that which has been salted only one year.

*Ans.* Have never tried it.

### GENERAL REMARKS.

*Question 1.* In my answer to this question, I have confined myself strictly to the "letter of the law," and have given you the best method of curing and packing beef such as is usually practiced in England and Ireland. Our packers follow this course only with such beef as is cut and packed expressly for the English market. The beef packed for sale in our own market, is packed into barrels directly after it is cut, the shortness of the packing season and the hurry consequent upon doing up a large business in a short time preventing the exercise of the proper degree of care, in fact it is mainly owing to the haste and carelessness incident to it on the part of packers of provisions, in this country that



so much of salted provisions turn out tainted or of inferior quality. The kind of salt used, has in reality much less to do with it than is generally supposed.

*Questions 6 and 7.* I would add to the causes of the softening of the rind of pork, the degree or extent of the *scalding* process. The water will necessarily be of variable temperature, and in many cases the hog may be left too long exposed to its action, and this would be sufficient to account for the change in many instances.

*Question, 11.* It was owing to the general use of fine salt in the interior and western part of our own State some years ago, and its invariable effect, upon pork and beef, when examined the spring and summer following, being as I have stated, that provisions so salted fell into disfavor, and the *prejudice* against the use of fine salt became general; at that time I think there was but a small quantity of solar salt manufactured. As the production of this latter quality of salt increased, the packing of pork in our State decreased, owing to the railroad facilities, enabling the farmers to find a better market for their hogs in New-York and Boston, so that at the present day there is little packing of pork or beef done west of the Hudson river, (Utica is the only point of any importance.) The packers on the river use exclusively foreign salt and have always used it.

The opinion that generally obtains, that Onondaga salt is not as good as foreign salt, is based upon the quality of that salt as manufactured years ago, and cannot be applied to the more recent manufacture of *solar evaporated salt*.

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Through your kind attention the following valuable and instructive letters have also been procured. They are from practical and intelligent men, and the clear and direct statements made, must commend them to the attention and confidence of all.

## PACKING PROVISIONS FOR MARKET.

LETTER OF THOS. F. DE VOE, ESQ.

NEW-YORK, Dec. 24, 1852.

B. P. JOHNSON, Esq., *Sec'y State Ag. Society*:

*Dear Sir*—I take this *late*\* opportunity of answering as far as I am able, the inquiries made by yourself and Pro. Geo. H. Cook, on the “curing of provisions,” &c. These subjects have commanded a part of my study and attention, as well as experience and observation for about twenty years past, as they pertain to a part of my business, and if what follows will be at all useful or interesting, it is most willingly given.

“The discoloration of (salted) provisions, particularly beef,” &c. You are aware, no doubt that the greatest quantity of “barrelled beef” sent to foreign markets, is packed in the heat; great portions are of young cattle, fattened on grass, principally of a quick and large growth, and are what we New-York butchers call “grass fed beef.” The beef when fresh will eat soft, tender, juicy and sweet, but will not have the delicious flavor, solidity or firmness, weight, or the heart or nourishment that stall fed (with grain) beef has. It appears to me as soon as the salt touches grass fed beef, it draws back, shrinks into a smaller compass, and changes to a dark color, as if there was not firmness or solidity to resist the action of the salt; and when boiled, especially if salted for a long time, will shrink very much, leaving it tasteless, juiceless, without heart or substance, and when cut of a dark color. “Stall fed beef,” on the contrary, is like corn-fed pork; it has the appearance (when properly cured) of being firmer, brighter, plumper, or has a swelled look, as if the well mixed fat protected the lean flesh. We seldom hear of farmers or others salting grass or milk-fed pork; they pen them up, and feed as much corn (generally) as the animal will take, for sometimes, months before slaughtering, and when they are salted, I quote an old saying, “put one pound of corn-fed pork in the pot, it comes out two,” which will apply to the stall-fed beef. Many cure with nothing

\*As I was at Washington, when your letter arrived, excuse this late answer.

but salt, (often bad tasted and dirty,) and the sometimes "muddy waters of our western rivers," which gives it a dark yellow and dead appearance.

I have seen a great deal of this kind opened for "Inspection," generally sweet ; but the beef had the appearance of having been taken from grass-fed oxen, steers, heifers and cows, of middling fatness, and but a small quantity of stall-fed and properly cured. Some years ago I put up, for the use of a trading ship in the Mediterranean, (and for several voyages) beef from stall-fed steers, 3 to 6 years old, (for I do not call them "oxen" until the animal is fully developed or grown, or until he has passed the age of not less than 6 years,) the plates, navels and brisket pieces ; took out all the bones and tied it in rolls of about 10 lbs. each, which I call "Scotch Roll," (and have sold quantities before and since,) curing with salt, sugar, saltpeter and spices. After being gone a long voyage, part came back as bright and handsome as the day it started, and always gave satisfaction.

Many persons ask, why it is that Irish (and also English) beef is preferred before ours? and of their using the name of "Ox Beef" and "Navy Beef?" The reason is, that their cattle are always, more or less, stall-fed on roots and grain, and are properly cured, with the best kinds of salt. Steers are seldom fed to that extent and length of time that the ox is. After the ox has become too old for work, he is stall-fed for (sometimes) months longer, as he fleshes and fattens slower than the steer, on the same quantity of food. Both are, however, strongly fed, as long as there is any improvement, then slaughtered, cut in pieces of 8 or 10 lbs. packed in casks nearly twice the size of our common provision barrels, and branded "Navy Beef," or "Ox Beef," or both. Our city (and eastern cities) cured beef, has always been preferred, and commands a better price than "Western Beef;" but the western packers are improving, as many English and Irish packers, within a few years past, have gone out there to put up for the English and other markets. I prefer steer to ox beef, both stall-fed ; because the steer's flesh, muscles, nerves, sinews, &c., are all young and tender, never having been called into the same action that the old ox has, who has worked and labored



until his flesh, muscles, &c. have become hard, tough, stringy and sometimes strong flavored. Give me prime stall-fed steers, four or five years old, strongly fed, not less than 6 months, the four quarters weighing between 800 and 1,000 lbs., good, sweet tight oak casks, Turk's Island salt, saltpeter and sugar, and I will make as good, clean, bright, sweet, good colored beef, and to keep as long as man could ask or wish for.

On "*the Discoloration of Cow or Heifer Beef.*"--There are so many causes for *discoloration*, and the different shades, that is, from a light to almost a black shade, that it is difficult to say, positively, without seeing it, or name the cause, but I will say that, generally, the cause of discoloration, is in the curing, (or handling, as the packers say,) and my reasons, as they occur to me, are; the grown animal, of packing qualities will not cause this dark discoloration, without it has been salted before the animal heat has left it, killed in a hot and worried state, or diseased. These are some of the causes. Some years ago I was often at an inspection and packing establishment, and I might as well give my reasons for being so often there. From information received from England, I was induced to "pack" above \$2,000 (as a trial) worth, of large heavy "stall-fed" cattle, say from 900 to 1,200 lbs., (4 qrs.;) cut and put it up, as directed, in tierces, containing 33 pieces, of about 8 lbs. each piece. The report and returns were, that it was just the thing wanted; but when all expenses were paid, I was a loser of about \$150, which stopped my packing: but to my reasons. A great many lots, from different packers, were opened for inspection. One in particular was very much discolored, almost black, and quite dirty; the beef about the usual kind "Barreled;" and to trace the cause was some trouble, but I wished to know it. It came from an irregular packer, who had used the steam boiled western salt, (Salina, I think,) a great deal too much, being about one bushel to every barrel; from 10 to 12 oz. saltpeter, and the not settled, dirty river water. You say that "the English packers say that this beef (cow or heifer) will always discolor." I think they must mean the flesh of small steers and heifers, about half grown, poor and thin in flesh; this kind of beef will be a shade darker than that of full grown animals, all salted in the same manner. The

flesh of the ox and cow, or full grown steers, is generally firmer, better beef color (red) than the young steer or heifer, (which is generally a dark veal color,) and of course will be a better color "salted."

The regular packer uses what they call "Solar salt," (ofttimes St. Ubes, or Bonaire, Turk's Island,) from 30 to 50 lbs.; about 6 oz. saltpeter to a barrel; and they have large vats, where the river water settles before it is used. Great quantities are sent to New-York, to be inspected and repacked; it is taken out, say ten barrels at a time, tried if sweet, thrown in different sections of a large circular bin around the scales, according to qualities, inspected and "Barreled" or repacked, using Turks Island, St. Ubes or Bonaire salt. The best quality is marked "Mess Beef," principally in barrels; the next best in tierces, marked "Prime Mess," 3d best, "Railroad" or "Prime," with the Inspector's name, which generally gives it character and sale.

Respectfully yours.

THOS. F. DE VOE,

Butcher, No. 7-8 Jefferson Market, New-York city.

J. AMBROSE WIGHT, Esq., editor of the *Prairie Farmer*, is entitled to our thanks for the valuable article annexed, on the packing of beef, and the discoloration of the meat in certain cases, and the probable cause. The English packers, at the Government Victualling Office, at Deptford, near London, insist that the beef of *cows* and *heifers* will *not retain its brightness*, but will grow brown or black. It will be seen (as we supposed it would) that the Chicago packers do not believe, from long experience, that the distinction of sexes affects the beef. The reason why beef is affected is clearly set forth in the annexed article.

B. P. JOHNSON, Esq., *Cor. Sec.*, N. Y. S. A. S.

We have questioned several of our largest and most experienced packers here, among whom we may mention Messrs. Thomas Dyer, O. S. Hough and J. P. Chapin, all of whom have been concerned in provisions for twelve or fifteen years, and are among the largest packers of beef in the world. Their opinions agree in the main, but vary somewhat as to unimportant particulars.

Not one of them has the least faith in any distinction between the sexes of cattle, as affecting their beef. On the contrary, they are all very sure, from positive experience, that no such distinction exists. All cattle will give beef liable to discoloration, under certain circumstances, and certain requisites are necessary in all cases to secure an article which will maintain its cherry color through several years of keeping. The wood of which casks are made is liable to affect the color. Oak staves, when green, contain an acid which is certain to act upon whatever the cask contains, and certain kinds of oak timber are more difficult to season than others, so much so as to be unfit for beef packing. Our casks, nevertheless, are made of thoroughly seasoned white oak or ash; and it is not probable that any difficulty arises from this source. The *burning* or charring the interior of the casks, sometimes colors the brine, but it is not thought to affect the meat.

But *the thing* which gives to meat the right or wrong color, is the pickle or brine in which it is kept; and the *principal ingredient* in the brine *which affects the color is the saltpeter*. If the quantity used of this article be *wrong*, the color *will not be right*; so say all our packers; nothing else will compensate for it. It is not meant that no difference will appear from poor beef, or beef which is rapidly falling away at the time of slaughter. Perhaps, also, beef killed when in heat after hard driving or violent exercise, *might* show it in the color, though the opinion is that it would not. But the circumstances here mentioned, are not supposed to occur in our beef-packing, in a sufficient degree to work any material change. The beef slaughtered here for long keeping, or the foreign market, is fatted on the open prairie, sometimes with the addition of a little corn, driven in by easy stages, and slaughtered when cool. But the greatest care is exercised in regard to all that affects the quality of the brine and the pickling of the meat. The best qualities of Rock, Turk's Island, or St. Ubes salt are employed. The precise quantity of saltpeter is added, and the whole is carefully scalded and skimmed three times, the meat being changed each time, before it is packed. Our packers for the English market have no difficulty in regard to the sale when the meat is thus put up.



There are many things which affect the color of meats newly slaughtered. As already stated, if an animal is killed soon after violent exercise, the meat will be dark colored, because the blood is driven to the surface by exertion, and only subsides to the interior by rest and coolness. Such meat will not keep well, because blood putrefies quicker than any other part of the animal. Pickling would very likely take out this extra blood, and then the color and quality of it would be right. But for immediate use, especially in hot weather, all animals ought to be slaughtered after rest. The color of moderately fed beef, especially that fed on grass, will be lighter than that highly fed or fattened on corn. The tallow of the latter, will, on the other hand, be yellow, and the color will be more particularly visible in the tallow; and this will be especially the case, if after high feed, some days of fasting be allowed to follow. The reason, perhaps, is, that stimulating food, such as corn, provokes a generous flow of the bile, which colors the meat more or less, and in the case of the suspension of food, this flow of bile would act still more effectively, since there would be nothing to absorb and carry it off. How far the color of corn itself will affect the meat, we are not prepared to say.

The following article is copied from the instructions to the master butchers, as given at the office of the Comptroller of the Victualling Office of the British navy. For the copy I am indebted to the kindness of the Comptroller, Thos. Grant, Esq.

*Mode of curing oxen and hogs, slaughtered in the establishment at Deptford.*

1. They are to be kept upon the premises and fed upon straw or hay for the periods mentioned in the following schedule, according to the time of their arrival at Deptford, in order to give time for them to cool, when they are to be killed and hung up in the slaughter-house twenty-four hours before they are cut up; at the expiration of that time the four quarters of each are to be weighed, and an account taken of the quantity thereof by one of the storekeeper's clerks. The marrow bones are to be taken out as clear of meat as possible, and the legs and shins cut off at the joint, or proper place, for which 16 lbs. in each are to be allowed. The remainder of each cwt. is to be considered as weighing 96

lbs., and is to be divided in the presence of the clerk above mentioned, and master butcher, into 12 pieces, in the most equitable manner possible, by cutting the prime pieces a little under 8 lbs., thereby allowing the other, agreeably to their coarseness and quantity of bone, to be over that weight.

2. After all the beef shall have been messed and taken account of as aforesaid, the whole quantity of kidney suet produced on the occasion, with as much of the head of the caul, as according to circumstances, may be requisite, together with the small pieces and scraps of meat which may be unavoidably produced in the cutting up, and the quantity taken account of in like manner, and the legs, shins, marrow-bones and scraps are to be delivered to the contractors, or otherwise disposed of as soon afterwards as possible.

3. The beef being cut up into mess pieces, as before mentioned is to be rubbed with white salt, and then stowed into the bins, occasionally throwing some white salt between the layers, where it is to remain the length of time mentioned in the following schedule, care being taken, for the more effectually hastening the cure thereof, that the brine which runs from the meat is thrown over it again, and repeated at least twice a day, covering the top pieces each time with white salt. For rubbing the beef, and sprinkling salt between the layers, and throwing some more daily over the pieces, while in the bins, after it has been washed off by the brine, and making pickle to fill up the casks, 1 lb. of white salt will be allowed for every 8 lb. piece of beef packed. After the beef shall have lain in this state, as above directed, it is to be carefully packed into barrels or tierces, each containing thirty-eight 8 lb. pieces, or in such other descriptions of casks as may be directed, with a proportion of 21 lbs. of bay salt and  $3\frac{1}{2}$  oz. of saltpeter mixed together, to every fourteen 8 lb. mess pieces of beef, which is to be distributed between the layers, as the meat is packed. The quantity of beef intended for each cask is to be weighed before it is packed, in order to insure that the number of pieces and the weight of the beef are the same in each cask of equal dimensions. The several casks are to be properly marked, for tracing the same, and ascertaining the contents thereof; the

casks are then to be properly coopered and filled with proof pickle, and transferred into the storekeeper's charge.

"4. The hogs slaughtered for the use of the navy are also to hang 24 hours, when they are to be weighed and cut up in the presence of the clerk and master butcher before mentioned, who are to take an account thereof in the manner already described, and every two cwt. of pork is in the same equitable manner as directed with respect to the beef, to be cut into fifty-five four lb. pieces, which is allowing two lbs. in a cwt. for waste. The pork is then to be well rubbed with white salt, and stowed in the bins, and treated in the same manner, and the like quantity of white salt will be allowed for its cure, and for making the pickle to fill up the casks containing the pork, as is directed with respect to the beef. When the meat has remained in the bins the time mentioned in the following schedule, it is to be packed into barrels or tierces, each containing eighty 4 lb. mess pieces, (or such other description of cask as may be directed,) with a proportion of 21 lbs. of bay salt and  $3\frac{1}{2}$  oz. of saltpeter mixed together to every twenty-eight 4 lb. pieces, which is to be distributed between the layers, as the meat is packed. The casks are then to be properly coopered and filled up with proof pickle.

"5. Every cask of pork is to have the necessary marks, &c., (as 3.)

"6. The tongues which may be produced from the oxen slaughtered in this establishment, are to be carefully cured in the following manner, viz: They are to be properly cleaned and then lodged on the racks in the tongue house to cool, as soon as taken from the oxen, where they are to remain until the morning appointed for cutting up the beef, when the tongues are to be well rubbed with white salt, and placed in a tub where they are to remain four days, at the expiration of this period they are to be taken out and again well rubbed with white salt, and replaced in the tub, without drawing off the brine, where they are to remain four days longer. The proportion of salt used in the operation is to be at the rate of 30 lbs. for every 60 tongues cured, and the



same proportion of salt will be allowed for making pickle for filling up the casks.

"7. The tongues being now considered perfectly cured, they are to be packed into such size casks as may be directed, with salt in the proportion of 9 lbs. of bay salt and  $1\frac{1}{2}$  oz. of saltpeter to one dozen of tongues. The casks are then to be headed up and made tight and filled with proof pickle.

"8. The suet which may be produced from the oxen slaughtered at this yard, is to be properly picked and lodged in places appropriated for drying the same, where it is to remain until the morning appointed for cutting up the oxen. It is then to be packed into barrels of 240 lbs. each, (or such other description of casks as may be directed,) causing white salt to be added thereto in the proportion of  $2\frac{1}{2}$  oz. to every pound of suet, which is to be distributed between the layers. The suet being packed, the casks are then to be properly coopered and filled up with proof pickle for which expenditure,  $2\frac{1}{2}$  ozs. white salt for each pound of suet will be allowed.

"9. The several casks containing tongues and suet are to be properly prepared, &c., (as 3.)

#### SCHEDULE

*Showing the days of the week when the oxen and hogs are to be sent into store from Smithfield market and other places; when they are to be killed; when to be cut up into mess pieces and salted, and when the said pieces are to be packed into casks.*

|            | When to be rec'd into the victualing office at Deptford. | When to be killed. | When to be cut up and salted. | When the mess pieces are to be packed. |
|------------|----------------------------------------------------------|--------------------|-------------------------------|----------------------------------------|
| Oxen,..... | Friday,.....                                             | Monday following,  | Tuesday following,            | Monday follow'g                        |
| Hogs,..... | Saturday,.....                                           | Tuesday "          | Wednesday "                   | Monday "                               |
| Oxen,..... | Monday,.....                                             | Thursday "         | Friday "                      | Thursday "                             |
| Hogs,..... | Thursday,.....                                           | Friday "           | Saturday "                    | Thursday "                             |

N. B. The meat is to be shifted from one bin into another on pack days, whenever the service will admit of it.

#### *Another mode of curing salt Beef and Pork.*

"The oxen or hogs are to be slaughtered after having remained two days on the premises, and to be salted the following day af-

ter they are slaughtered, and packed into casks ; after remaining in that state not less than 8 nor more than 10 days, the beef or pork is to be weighed and repacked.

“The quantity of common salt for salting and pickling a tierce of beef of forty two pieces of 8 lbs. each, is to be 42 lbs. bay salt, for repacking 84 lbs. The quantity of common salt for salting and pickling pork, the same as that for beef, but the bay salt only 70 lbs. to each tierce.

“Half a pound of saltpeter to be used to each tierce of beef or pork ; a quarter of a pound to be used in the first salting ; and a quarter of a pound when the meat is repacked.

“The casks to contain 38 pieces of beef of 8 lbs. each, or 40 pieces of pork of 4 lbs. each, exactly of the same dimensions as the Irish India tierces, if not, the quantity of salt above mentioned must be regulated in proportion to the size of the cask.”

These instructions are dated Jan. 2d, 1838. Since that time, however, the system is changed, the salted meats are supplied by contract ; the stipulations in the contracts being nearly the same as in the above instructions.

The nature of my investigations has been such, that I have been extremely desirous to know if there was any inferiority in the quality of the salt made at Onondaga, in our own State. From what has been stated in the preceding part of this paper on the various circumstances which affect the curing of salted provisions, and on the powerful prejudices which exist in the minds of men, relative to different kinds of salt, as well as from a careful chemical analysis of a great many varieties, I conclude that it is not inferior to any other, and in point of cleanness it is decidedly superior to all others. My conclusions are sustained by the census reports of the butter and cheese made in this State. The State of New-York furnishes about one-fourth of all the cheese made in the United States, and of the 79,000,000 pounds made in 1850, the larger part was salted with Onondaga salt. The character of this cheese in our own and in foreign markets, is of the highest kind.

“In relation to the manufacture of cheese in this State, from an examination of the various dairymen who have presented cheese

for exhibition at our various fairs, I am satisfied that more than two-thirds of them have used the salt manufactured at our own works. The character of our cheese abroad, in England particularly, is such, that our best cheese brings in the Liverpool and London markets nearly equal prices to the very best cheese manufactured in the best dairy districts of England.

B. P. J."

In the preservation of beef and pork I could cite the testimony of numbers of packers, but the following from Mr. Slocum, of Troy, is sufficient. It was written three years ago, (Assembly document No, 184, page 40, of 1850,) but in an interview with him since, he assures me that his further experience has only confirmed him in the opinions then expressed. He then testified "that for the last fourteen years he had been extensively engaged in packing beef and pork in the State of New-York, and for the last five years has packed beef and pork in Ohio and Illinois, say more than ten thousand barrels in each year, two-thirds of all which has been packed in the Onondaga coarse salt. And deponent says that he would as soon use the coarse Onondaga salt for packing beef and pork, as any foreign salt, and that he knows from experience, that the Onondaga solar salt will save beef or pork as well as any foreign salt, (Turk's Island, St. Ubes, or Bonaire,) notwithstanding the fact that he could purchase foreign salt as cheap as he could get the Onondaga salt, at Peoria and Chicago, he has used nearly all of the Onondaga salt at those points; he has packed fifteen thousand barrels of beef and pork at Huron, Ohio, in the last five years, entirely with the Onondaga coarse salt, all of which has kept as well as the same quantity packed in this country with Turk's Island salt; he has packed more than fifty thousand barrels of beef and pork with Onondaga coarse salt as well as any one could have done with foreign salt. My beef has been mostly sold in New-York, some in Boston and some in New Bedford. It has brought as high a price as any beef of the same quality packed with foreign salt. I have not packed any beef for the English market which is usually of better quality than we pack for the home market. My experience is, that the Onondaga coarse salt does save the beef and pork as well as any foreign salt, and does not discolor the meats in the least."

(Signed,)

HIRAM SLOCUM."



The following statement relative to the packing of pork, is quite to the point. It was written by one in whose judgment I have entire confidence, and I can confirm his statement of the appearance of the two kinds of pork from my own observation :

WASHINGTON, *January 30, 1853.*

It is known to the public that the Secretary of War, a year ago, ordered experiments to be made in packing pork, to test the relative qualities of Onondaga solar salt with Turk's Island. Each hog was cut in two on the back, and one half packed with Onondaga solar and the other half with Turk's Island salt. The same quantity of each kind of salt being used in each case, and packed in barrels of the same quality. In short, the treatment of each kind throughout was the same, in all particulars. This pork has been packed for more than 13 months, and a few days since I saw some of it opened, and it was impossible to discover any particular difference between the two kinds of salt, or to see any difference in the quality or preservation of the meat.

The pork was put into barrels numbered from 1 to 100. The odd numbers being of one kind of salt and the even numbers the other. They were sent out, one of each kind, to every military station throughout the United States, with instructions to be opened after a given time, and certain tests of the meat to be made by a board of officers, under the direction of the officer in command. Many of these reports have been received at the Commissary's office, and yesterday I took occasion to examine them. The result is, that it is almost impossible to discover any difference. The greatest is in the loss of weight, after being boiled for an hour and a half. As a general thing, there is more loss in weight in that salted with Turk's Island, than with the Onondaga solar salt. In most cases, the meat is represented as being uncommonly good. The result of this experiment thus far, is a full vindication of the quality of the Onondaga solar salt, and shows beyond a question that it is fully equal in all respects to the best Turk's Island brought to this country for packing purposes.

In the salting of butter with the different kinds of salt it is more difficult to get clear ideas. The whole is so entirely a matter of *taste* that one can hardly dispute anything that may be

said on the subject. I do know however of a large number of cases in which the most skilled have failed to distinguish one from the other, and of many other cases in which the "knowing ones" have shown themselves most entirely mistaken. Excellent butter is made in those parts of this State where Onondaga salt is used, equal I have no doubt to that where foreign is made use of.

To the above may also be added the following from my report to the Superintendent of Onondaga salt springs, last year :

"The various charges made against Onondaga salt, are most varied in character, and many of them exceedingly vague in their statements. Large quantities of provisions are undoubtedly spoiled every year, but there is no testimony to show that more are lost by the use of Onondaga than of other salt. Still, if they are spoiled or injured, and some cause must be assigned, there is none more convenient than bad salt. It is undoubtedly true, that provisions will spoil if an insufficient quantity of salt is used. It is also true that salted meats frequently spoil, though enough salt is used, if they get out of the brine and are not covered with salt, and in hot climates they even spoil when covered with brine, if there is not a plenty of salt over them."

Knowing that the English Cheshire salt was very much like Onondaga salt in purity, and that it was all made by artificial heat, I addressed a letter of inquiry to B. P. Johnson, Esq., Secretary of the New-York State Agricultural Society, at that time in London, as Commissioner from the State of New-York at the World's Fair. The following is his answer :

LONDON, *July 29th*, 1851.

"Prof. Cook :

The following information I obtained from the most extensive packer of provisions in London, and it is entirely reliable. From what I learned from the provision dealers in London, on the subject of the practice in Ireland, I am led to believe it is substantially the same as in London.

Very respectfully yours,

B. P. JOHNSON,  
*Commissioner State of New-York.*

No. 10 BURY STREET, ST. JAMES }  
 July 14th, 1851. }

ROBERT HASTIE, ESQ. :

*Dear Sir*—I am desirous of ascertaining from some of your provision dealers, answers to the following questions ; and could you obtain them for me without too much trouble, you would greatly oblige me.

Respectfully yours,

B. P. JOHNSON.

1. Is Cheshire salt used for packing provisions for the army and Navy of Great Britain, and is it used in the fisheries ?

A. St. Ubes bay salt for the heading of provisions and Liverpool salt for packing, and a coarse description of the same is used in the fisheries.

2. Are the discolorations of provisions which sometimes occur attributed to the salt or to the wood of the casks ?

A. To the salt only.

3. Is it true that the deliquescent chlorides in salt are not injurious to butter or cheese ?

4. What are the most approved salts for packing provisions and for household use in the English market ?

A. The large salt merchants in London, say that beef or pork for the navy are salted with the coarse, or common salt, and the casks are generally headed up with St. Ubes bay salt, and there is a finer description used for butter, and known as butter salt, and the fine stoved salt is used for household purposes ; and all these salts are obtained from salt springs.”\*

With regard to the discoloration of provisions spoken of above, it has frequently been observed, and many persons attribute it to the salt ; Stephen Smith, Esq., of Syracuse, many years since asserted that the color was from the wood of casks. A writer in the report of the Commissioner of patents, for 1843, p. 221,

\* The different names are applied to the Cheshire salt on account of the different temperatures at which it is made, and consequent difference in the size of grain.



writing from Liverpool to direct American provision dealers in packing for the British market, also states that such is the case. A provision dealer of great experience, assures me that he has frequently observed the same fact. To test the matter I salted beef with salt in which oak saw dust had been mixed, and then kept it at a temperature of about 70° for a few days; it became of an inky black color on the surface; the color was brightened by boiling. The same effect was observed both with foreign and domestic salt.

From these facts I cannot but conclude, that much of the prejudice which exists against Onondaga salt is unfounded. Good salt is unquestionably desirable, and, if the objections which have been made against the present article should lead to the manufacture of a better, both manufacturers and consumers will be benefited. There appears to be some misapprehension as to the use of the different kinds of salt; many persons supposing that if equally pure, they are equally well adapted to different uses. Such however, is by no means the case; very fine salt is best for culinary purposes, and that which has the largest amount of chlorides of calcium and magnesium is preferred on account of its sharper taste. That which will dissolve quick is always the safest for salting meat in warm weather, because it *strikes* quickest. A portion of coarse and heavy salt at the top of a barrel of provisions is desirable, for it keeps the brine strong at the surface and thus hinders it from souring. These and other facts of a similar kind may serve to explain some of the objections which have been made to different varieties of salt.

The above cited facts it appears to me are sufficient to present the subject of *curing and preserving beef and pork* in its true light. Many facts on the *curing and preserving butter and cheese*, have been collected, but they are not yet as complete as I should like to make them. Should opportunity offer I hope to present them more complete at some future time.

Hoping that these may prove useful to the great interest to which you have devoted yourself,

I remain, very respectfully, Yours,

GEO. H. COOK.

ALBANY ACADEMY, }  
Albany Feb. 9th 1853. }

REMARKS

UPON

ALCHYMISTS,

AND THE

SUPPOSED OBJECT OF THEIR PURSUIT; SHOWING THAT

THE

Philosopher's Stone,

IS A

MERE SYMBOL, SIGNIFYING SOMETHING WHICH COULD NOT BE  
EXPRESSED OPENLY WITHOUT INCURRING THE  
DANGER OF AN AUTO DE FE.

---

BY AN OFFICER OF THE  
UNITED STATES ARMY.

[PRINTED FOR PRIVATE CIRCULATION.]

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CARLISLE, PENN'A.  
PRINTED AT THE HERALD OFFICE.

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815.17

Wm. Brewster, Esq.

Aug. 7. 1867.

# Advertisement.

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TO MY FRIENDS IN PARTICULAR, AND IN GENERAL TO ANY ONE WHO MAY  
FEEL DISPOSED TO LOOK INTO A SUBJECT OF NO LITTLE INTEREST,  
REGARDED FROM ANY POINT OF VIEW WHATEVER :

I present you in this little pamphlet a simple account of what appeared to me a discovery in regard to the Alchymists, or the object of their labors in pursuit of the Philosopher's Stone. This class of men, scattered through many ages, usually call themselves Hermetic Philosophers, or disciples of Hermes Trismegistus; but from the terms commonly used in their works, they are generally styled Alchymists, and sometimes Spagyric Philosophers, while from their great knowledge of nature and her operations, many of them have been regarded with fear and dread as Magicians.

I have not attempted to make a book, and from want of skill in literary composition I have fallen into an easy mode of statement, by using the personal pronoun, not to obtrude myself upon the reader, but simply because I found it the most convenient and ready way of delivering what I had to say.

E. A. HITCHCOCK,  
U. S. Army.

*Carlisle Barracks,* }  
- March, 1855. }





## Remarks.

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SOMETIME in July, 1854, having then but recently returned from a tour of Army duty on the Pacific coast, I strolled one day into Bangs' Auction Bookstore, in Chatham street, New York, where I saw spread out upon a table a number of books catalogued for sale that evening. They were so placed that their titles could readily be seen, and I observed among them a small volume with the word "*Arcanum*" on the back of it. What hidden matter, said I to myself, can be in this little volume—at the same time taking it up and opening it at random. I saw at once that the subject of the volume was *Alchymy*, though the first half of it was taken up with what was called (at the top of the page) "Chymical Collections," while the second half was styled "Hermetic Secrets," and in this last portion I supposed was contained that which gave the title to the book. I examined, then, the title page, which ran thus—"Arcanum, or the Grand Secret of Hermetic Philosophy, wherein the Secrets of Nature and Art, concerning the matter and manner of making the Philosopher's Composition, are orderly and methodically manifested. *The work of a concealed author.*" It was the third edition, and by the date at the close of the preface was published in 1650.

A spirit of curiosity seized me and I thought I would leave a limit bid for the book, in order to see what the writer had to say about Alchymy, and about the Hermetic philosophy. Accordingly I desired a clerk in the establishment to bid, not exceeding two dollars for me, the book being a little, old, sheep-skin bound volume, which if judged by its size and appearance might not bring on sale over a fourth of a dollar. The next day I called to inquire after the result of the sale, and found that the book had been struck off to me at one dollar,

which I paid and immediately stepped into a *car*, then about to start from the lower end of the Park for Fourth Avenue, where I had taken lodgings in the Clarendon Hotel. As there was nothing in the streets through which I passed to attract my attention, I soon opened my little *Arcanum* book and began to read the preface (the "*Prolegomena*," as 'tis called) and in a very few pages, I might almost say lines, I discovered that the object of the Alchymists *was not* a veritable Stone of any sort, and that they were not in search of means by which metals might be transmuted into gold; but that the Philosopher's Stone was a mere symbol of something else, and my first impression was—and this has not been materially changed since, though it has been somewhat modified or perhaps I should say defined—that the Philosopher's Stone is the symbol for Wisdom; and the problem of the Alchymists is, how to attain it.

The anonymous writer of the "*Arcanum*," like all of his tribe, has published nothing openly, and if my reading had been confined to this single volume I should have nothing to say about the Alchymists; but by reading this little work I was induced to inquire at Gowan's store of old books in Fulton street, and to my surprise and satisfaction I found over half a dozen volumes, old, worm-eaten, worn and soiled, with odd titles, which I had acquired just wit enough from the *Arcanum* to see related to the same subject; to wit:—Alchymy and Hermetic Philosophy, for these are two names for the same science or subject.

I immediately began poring over these strange books with an increasing interest at every step, as I saw more and more clearly that the Hermetic writers, as they prefer to call themselves, whether right or wrong, were an earnest, truth-loving people, in the highest degree disinterested, most of them writing anonymously, and all of them wrapping around their doctrines and opinions a dense cloud of mysticism, no where in direct language stating their object, though again and again cautioning their readers that their meaning was not on the surface, and could not be reached but by an earnest endeavor, which must also be crowned with the blessing of God, without which, it appeared, no one could by any possibility discover the Philosopher's Stone; and moreover, they warn every reader who is fortunate enough to discover the "great secret," which they often speak of as divine, not to disclose it, the preface to the "*Arcanum*" closing with these ominous words—"I charge all those that shall reap any benefit by this translation, under the secret and severe curse of God, that they bestow upon it the August Reverence due to such a secret, by conceal-



ing it to themselves, and making use of it only to the Glory of our great Creator."

The Arcanum, I ought to say, is a translation into English, the preface being by the translator,—one James Hasolle, whoever he was.

I must hasten now to take myself from under the dreadful malediction invoked upon whoever discloses the grand secret, and this I can do without the slightest difficulty; for although I have said that the Philosopher's Stone is but a symbol of wisdom, I have not attempted to say what wisdom is, and therefore do not feel the least apprehension of the dreadful consequences of betraying the secret of the Hermetic writers: and in truth, I am as safe from incurring the terrible penalty as Hotspur's wife, who, it was certain, could not betray what she did not know.

I repeat then, that the Alchymists were not, and I am not forbid to say what they were not, in pursuit of a composition of any sort by which metals might be transmuted into gold; but the "Stone" of the Philosophers, as also their "*Elixir*," or "Universal Medicine," for these are all one and the same thing, had reference to *man*,—to his perfection and salvation.

It will no doubt be asked, why make so profound a secret of what all men must necessarily have an interest in? Why not call things by their right names, and treat openly of matters of the highest concern to man? But let us be patient: possibly the reason for this secrecy is a part of the secret, and by a little industry we may find out something that may reward us. We all know why Socrates was compelled to drink the hemlock, and it has been said, not without some probability, that if Christ were to appear again in some parts of the christian(?) world he would be crucified over again. Don't let us be in a hurry to get at the bottom of this matter. It requires some little time to master any ordinary science, even that of arithmetic, and if wisdom, or something like it, was the object of the Hermetic writers, we may be sure their secret is not to be compassed in a moment.

✧ I will now proceed with my simple statement of facts. Among a few volumes that I happened to have in California, was an old work in English by Van Helmont. I had read the volume without being able to make anything of it, and had given it up as a thing of strange vagaries about the "atmosphere," and about "water" and "quicksand;" and how the latter underlies all things, and is contained in all things—never once dreaming that by quicksand the writer had sym-

bolized the Spirit of God. But instructed by the "Arcanum," and by the few books found at Gowan's, I remembered Van Helmont, and on turning again to his volume I found myself in the very heart of Hermeticism, and read "The Paradoxal Discourses concerning the Macrocosm and Microcosm, or the Greater and the Lesser World and their union," (for this is the title of the book) with an extraordinary interest, somewhat assimilated possibly to that of gold hunters who chance to light upon a good sized lump of metal nearly pure. There would appear to have been two Van Helmonts, father and son, both of them Hermetic writers; for besides the "Paradoxal Discourses" in one volume, published in English in 1685, there is another volume published in 1650, which I suppose to have been written by the elder Van Helmont. It is entitled "Deliramenta Catarrhi, or the incongruities, impossibilities, and absurdities couched under the vulgar opinion of Defluxions. The Author, that great Philosopher, by Fire, Joh. Bapt. Van Helmont; the translator and paraphrast, Dr. Charleton, Physician to the late King." This same volume contains also what is entitled "A Ternary of Paradoxes," in the Hermetic style, the reader of which, if he sees nothing else, will be astonished to read what is said of *magnetism*, in view of what is urged in these days under various names, as clairvoyance, spirit-rapping, &c. All I have to say of this work is to recommend its study. If it does not give out its own meaning clearly, it may help the reader to get at a better understanding of his own view of things. It must be admitted that symbolic writing, (witness Goethe,) admits of a variety of interpretations. Dante has pointed out three, as I perceive by an extract from his *Convito*, distinguished from each other essentially. But I do not design a discussion of this matter. There is a great deal of meaning in Van Helmont, and every reader may find something to his purpose; just as in nature, many people find or think they find in that Proteus just the very thing they seek.

If I were asked what single book I would recommend in order to teach something of the Hermetic philosophy, in English, I think I should name a small volume (nearly all of these people write in nut shells) entitled—"The Hermetical Triumph, or the Victorious Philosophical Stone.—A Treatise more complete and more intelligible than any yet published, concerning the Hermetical magistry, translated from the French. To which is added The Ancient War of the Knights, translated from the German original," &c.—published in 1723. This volume with the dialogue included in it between Eudoxus and Prophilus, almost tells the story; but it requires reading and re.

reading, very slowly and thoughtfully: for it must be observed that when symbolism undertakes to set out nature, no progress can be made in understanding the real meaning without some knowledge of nature. If a picture is shown us, how can we judge of its likeness if we know nothing of the original? It is so in all things, even in logic:—a man can only understand books on the art or science of logic, by being able himself to reason. In like manner grammar is an art which does not make, but only records the rules of speaking and writing, which rules have an independent existence giving the law to grammarians or their books will be “foolishness.” If, in order to progress in these subordinate studies, the student must bring something himself to the study, it need not be considered strange that the rule holds good in the study of Hermetic philosophy. By the time any one reaches even a definition of this philosophy, he will begin to understand what the Alchemists meant by their “Stone”—which, it is important to observe, has not one, but several meanings, according to the connection in which the word is used; just as a piece of rude native mineral ore is one thing as it comes out of the mine, and quite another when, after being refined and wrought upon by art, it adorns a lovely virgin zone at a marriage ceremony, in the form of a beautiful brooch. But I do not undertake to say what the “Stone” is, but only what it is not; and I repeat that it is not a metal at all, nor has it anything to do with metals except to teach their true value; and whatever be the value of gold, that which teaches its true uses must be of more value.

I wish also to say that with an extraordinary similarity in the main, these writers are wonderfully varied in their modes of presenting their doctrine, yet never for an instant throwing aside the mask. I have one small volume entitled, “Nature’s Explication and Helmont’s Vindication. Or, a short and sure way to a long and sound life, &c., &c., by George Starkie, a Philosopher made by the fire [this has a meaning] and a professor of that Medicine which is real and not Histrionical,” published in 1657. Here the diseases of the soul are treated under the similitude of those of the body and a certain “universal medicine” is indicated—for the benefit of those who can discover it. This medicine has a wonderful power over natural things according to Starkie; for example, the author says:—“The most abstersive simple that I ever knew in the whole vegetable kingdom is Opium”—

[“The weariest and most loathed worldly life,  
That age, ache, penury, and imprisonment  
Can lay on nature, is a paradise  
To what we fear of death.”]



which of itself is a deleterious narcotic venom, but by means of this elixerated Salt, [the Philosopher's Stone] it loses all its odious qualities, and becomes a most powerful sudorific, eminently *anodynous*, and cures all fevers though never so acute: In the preparation of which it is observable, that only a *feculent sediment* is separated, and the rest is turned into a *volatile salt*, which is not excelled in the whole vegetable family. \* \* \* Happy is that physician [Soul doctor] who knows how to separate the deadly qualities which are in *opium*, so that it may retain its virtue of acting upon the Duumviratus. For this simple, thus corrected, by its innate specific quality, doth work on the seat of life, purifying the *archeus* without the least stupefaction, but rather *keeping the patient awake*. \* \* \* The same way Hellebore corrected is a noble remedy against lingering *quartans* [people shake and tremble from more causes than one], and so I could instance in very many simples, but time will not permit my enlargement here. \* \* \* And by way of admonition to our wise masters in this science, I shall remind them, that in the whole vegetable family there is not a simple so *diaphoretic* as *opium*, which they account of all vegetables the most cold; in which let them learn from me, that the *narcotic* virulency may be separated, without altering the specific virtue in the least, and then it is *anodynous with much pleasure to the patient*."

Here I have before me no less than seven different treatises on Alchymy in one volume, prepared in English, by translations from the Latin, by William Salmon, and published in 1691. It is entitled "Clavis Alchymiae." I ought to have given this volume the preference over the "Hermetical Triumph," though in all these books without exception, one needs a *hint* as an entering wedge; for the "Clavis" needs a *clavis*. Nearly every writer professes a determination to be more explicit than any of his predecessors, and the reader commences with high hopes that, now, indeed, he is to reap satisfaction; but as in reading Meno on Truth; Alcibiades on Justice; Philebus on the Good; Theætetus on Science, and so of many others of Plato's Dialogues, if the reader expects to be supplied with knowledge while he "reclines half a sleep on a bed of down," he will be mistaken. The true rule is stated in Philip, 2. 12.

The seven treatises prepared by Salmon are contained in the second and third books of his volume, the first, in my copy, having been lost. One of these treatises is by no less a person than Roger Bacon, the gunpowder man, whose knowledge of nature made him the dread of his own age (as a magician) and the wonder of all succeeding times:

and here I must say a word of a book recently published (1852) in England, by Charles Mackay, L.L. D. entitled "Extraordinary Popular Delusions," in which the really learned author has devoted a large portion of one volume, over a hundred pages of close print 12 mo., to the Alchemists, preceded by a suitable plate representing an old bearded codger, seated, half doubled, blowing the coals under his alembic, intently watching the process of making the "Stone," or the "medicine." In this history of the "delusion" of the Alchemists, Mr. Mackay has given a sketch of the lives of some forty men devoted to Alchymy, of extraordinary genius, according to his own account, without once entertaining a suspicion that they might have had a really important and legitimate object, although he has made many quotations from their works the very absurdity of which on their face, one would think might have suggested the possibility of a concealed purpose. Of Roger Bacon, Mackay says—"In a history of Alchymy, the name of this great man cannot be omitted, although, like many others of whom we shall have occasion to speak, he only made it secondary to other pursuits. The love of universal knowledge that filled his mind, would not allow him to neglect one branch of science, of which neither he nor the world could yet see the absurdity. He made ample amends for his time lost in this pursuit by his knowledge in physic and his acquaintance with astronomy. The telescope, burning-glass, and gun-powder, are discoveries which may well carry his fame to the remotest time, and make the world blind to the one spot of folly—the diagnosis of the age in which he lived, and the circumstances by which he was surrounded. His treatises on the *Admirable Power of Art and Nature in the production of the Philosopher's Stone* was translated into French by Girard de Tormes, and published at Lyons in 1557. His *Mirror of Alchymy* was also published in French in the same year, and in Paris in 1612, with some additions from the works of Raymond Lulli." Mr. Mackay, after some account of Lulli, commences his notice of Bacon in these words:—"The powerful delusion of Alchymy seized upon a mind still greater than that of Raymond Lulli. Roger Bacon firmly believed in the Philosopher's Stone, and spent much of his time in search of it." And why not, if under the name of Alchymy and the pursuit of the Philosopher's Stone, he meant the perfection of man and his salvation? But, again, it may be said, why not speak out? Why keep up a perpetual gabble about Salt, Sulphur and Mercury (spirit, soul and body) and about solution, calcination, (repentance) and fifty other things implying the use of hot coals and a blow-pipe? But again, I repeat,

let us be patient, for while the Alchymists were at work with their fire there was another sort of fire burning almost all over Europe, kindled and kept in a terrific blaze by a class of men called Inquisitors, who had taken out a patent for salvation after a stereotyped method; and besides, we may believe there were other reasons. Are we of so little faith in such men as Roger Bacon as to believe they would put a visor over their faces unless there was need of it? If we cannot believe in this necessity, let us just for experiment sake, "suppose this supposition," and then study the works of the men who made themselves invisible by means of it except to their true and competent friends.

I have been turning over the leaves of Salmon's translation of the works of Hermes, Kalid, Geber, Artephius, Flammel, Bacon and Ripley, hoping to find something by which to indicate their object, but it is much like seeking the commencement of a circle. There is no reason for selecting one thing rather than another, for all things are so bound to all that a preference can hardly be fastened upon any one thing. But here, at page 265, is something from the translator in praise of the "Stone." "Possessing this Stone," says he, "thus perfected, you possess all the wealth and treasures of the world; so that you may live free from care and fears; from every-sickness and disease: It is a remedy for all diseases both of body and mind: It strikes at the root of infirmities; and destroys that which would destroy or undermine the health and prosperity of the human body. This Stone, this wealth, this treasure, though it be but like a *grain of mustard-seed*, yet it grows to be the greatest of all trees, in whose branches the birds of the air make their nests, and under whose shadow, the beasts of the field dwell."

In reading such a description of the Philosopher's Stone, let the student hold himself in silent contemplation a while, under the self question: Is there anything in the universe of which this can be said? or, what is that, in the universe, endowed with, or possessed of such extraordinary properties?—and if he can find out what it is, he has found the Philosopher's Stone, for this is but a mere name of something, the *thing* being indicated not by the name, but by the properties attributed to it. No sensible man need be told that God may be called indifferently, "Jehovah, Jove or Lord."

But I am in no danger of disclosing a forbidden secret, for a reason already given, yet at intervals I feel disposed to reiterate, that "the Stone is not a Stone;" except that, figuratively, the heart of man is sometimes said to be hard and stony, and before it can be made



accessible to the elixir or spirit, it must be softened and become even as that of "a little child," and thence be purified, passing through three states (the Alchymists say), the Black, the White, and the Red state, (repentance, sincerity and the fruits of righteousness). But I will say no more of Salmon's book except to recommend it to those who can find it, though I fancy this will not be easily done.

Another work before me is by a Venetian, *Otto Tachenius*, in two parts, the first, entitled, "Hippocrates Chymicus, discovering the Ancient foundation of the late *Viperine Salt*, [?] with his clavis thereunto annexed, translated by J. B.," 1677. The clavis itself, the second half of the volume, is entitled "Clavis to the Ancient Hippocratical Physick or Medicine, made by manual experience in the very fountains of nature, whereby through fire and water," &c., &c. This is the work of a learned and earnest man but I have not mastered it.

In 1650 and 1651, there were four or five separate works published on Hermetic Philosophy by Thomas Vaughn, under the name of *Engenius Philalethes*, for which he was duly abused by Henry More, and others. These works are all interesting but should be read with some caution and reserve; for although they seem to be the production of an ardent lover of truth, yet they indicate some want of completeness in knowledge, and are the only books on the subject I have yet had in hand which exhibit some little asperity and spirit of controversy, brought out by an attack upon him; the writings of the masters, being entirely free from all blemish in these respects. It is impossible not to catch something of the calmness pervading their works while reading them. They seem all of them to have taken a stand above the chances and changes of fortune, as if they had laid hold of the eternal and could in no wise be drawn into the whirling vortex of the transient. Vaughn's works are all very small but remarkable volumes, read with the caution I have indicated. They are entitled—1st. "Anthropozohia Theomagica and Anima Magica Abscondita (in the same volume); 2d. Lumen de Lumine, or a New Magical Light discovered and communicated to the world; 3d. Magia Adamica, or the Antiquity of Magic," &c.

I have one small volume in French, made up of three treatises, one from Hermes, whose name is among the greatest, and indeed from whom the philosophy itself was named; then, one from Bernard count de la Marche Trevisane, which is a model in its way; and lastly "La Chrysopée de Jeant Aurelle Augurel, qui enseigne l'art de faire l'or," which last is in verse, the merits of which I would not like to pronounce upon.

Another work in French and exceedingly valuable is by Le Sieur de Nuisement (1621) and is entitled "*Traitez du Vrai Sel.*" [If he had entitled his book, a treatise on God, some readers would have supposed they knew all about the subject before opening the book; but as he wrote about Salt, that is quite out of the way and very Hermetic. This book is said on the title page to be "a very useful work to whoever desires to attain a perfect practice in the precious elixir or universal medicine," &c.

I have three other volumes, in French,, by Antoine Joseph Pernety one being a "*Dictionaire Mytho-Hermetique,*" published in 1758. In the other two, published in 1786, the author attempts to explain some of the principal Egyptian Fables in accordance with what may be called the Hermetic Theory, but still in the Hermetic cypher; and it cannot be denied that he has shown great ingenuity and learning. If he has not succeeded in his purpose he has come as near to it as most others who have attempted to explain the same fables on a variety of different theories. Osiris, Isis and Horus, are in this theory, salt, sulphur and mercury; for it must be stated that the Hermetic philosophers are Trinitarians, though perhaps hardly one of them would be willing to confess to the name without the privilege of making his own explanations. Typhon, also, is not forgotten in this system, and it is quite refreshing to see how badly the villain is used and finally disposed of. The Dictionary of Pernety needs a Dictionary; for like all other Hermetic books, it is mystical, obscure and symbolical; but is nevertheless very valuable, for in this sort of writing one book helps to explain another, and I may as well say at once, that it is quite impossible to penetrate the meaning of these works by reading any one wholly by itself.

Another work well worth reading in connection with this subject is a "*History of Magic, by way of apology for all the wise men who have unjustly been reputed Magicians, from the creation to the present time*"—written by G. Naudæus and published in English (from the French) in 1657. I am inclined to believe that the author was himself a Hermetic adept, though he no where declares it. His book is written at all events, with great spirit, learning and independence.

Besides the works I have named and which are in my possession, I find a number referred to in the *Hermetical Triumph* and in other works, as valuable, which, as yet, I have not been able to obtain; among them are the *Turba*, *Rosary*, *Theatrum*, *Chymical Cabinet*, *Arnold de Villa Nova*, *Raymond Lully*, *Zachary*, *Basil*, *Valentine*, *Cosmopolita*, &c. After commencing with almost any one, the reader

is readily led to the knowledge of others, though it may be difficult to find the works themselves. They are not to be had in ordinary book-stores, but only with dealers in second-hand books, accumulated from the breaking up of libraries and their sale, often on the death of their owners.

I believe I have now told my story, such as it is, yet I feel like saying a few last words.

I have been very strongly drawn to these mystical writers about serious things. I find no spirit of dogmatism in them. They are one and all serious, earnest and learned men, taking their cue not from human authority, but from the source of that authority, and when they quote each other it is but to illustrate and not to establish a position by the credit of a name. I cannot but be impressed with the strangeness of the fact, that for whole ages (they quote writers of their own stamp behind Plato) there have been a peculiar and distinct class of men, very learned and ingenious, wholly bent upon something from which neither honors, nor profit, nor pleasure, could withdraw them; living obscurely and dying, many of them, entirely unknown and as if they preferred not to be known; for their books are often anonymous, and the reader is not informed of a single fact about many and indeed most of the authors, except what his own ingenuity may draw inferentially from the doctrines promulgated, in which exercise greater skill is required than that of Cuvier, who, with a single bone, 'tis said, could re-construct the frame of the animal from which it came. These men seem almost to address us from the other world, as if they had taken leave of this, and desired only as angels may be supposed to be moved, to assist us all in their power, without the possibility of being aided in return.

Still, the question recurs, why this extraordinary secrecy? But this secrecy is much older than is generally supposed and occupies a wider space in literature than is commonly known. There seems but little reason to doubt that *Heraclitus* wrote expressly in this secret language. The following lines, intended no doubt for verse, were written of him and may be found in Bohn's Edition of Diogenes Laertius.

"Be not too hasty, skimming o'er the book  
Of *Heraclitus*; 'tis a difficult road,  
For mist is there, and darkness hard to pierce.  
But, if you have a guide who knows his system,  
Then everything is clearer than the sun."



Heraclitus is represented as speaking from his tomb thus:—

"I who lie here am Heraclitus; spare me  
Ye rude unlettered men: 'Twas not for you  
That I did labor, but for wiser people!"

From the days of Heraclitus to the present time, there have been writers who have published nothing openly, but have exhibited what they had to say in some sort of foreign dress, as in fables, allegories, enigmas and parables, by which one thing has been said and another meant.

I have but small respect for his penetration who cannot see, especially when it has been once pointed out, that Dante in his *Vita Nuova*, under the form of a human love has exhibited the experience called the new birth in religion. This same experience makes the subject of that inimitable poem, translated in part by Chaucer, called the Romaunt of the Rose. I learned to read this sort of writing understandingly from *Rossetti*, whose "Discourses on the anti-papal spirit which preceded the reformation," though the mere theoretic part seems carried to extreme, is undoubtedly a living work, and the only key to Dante, Petrarch, Boccaccio and many others who wrote of *Love*, without at all meaning what commonly passes under that name. Yet of the "Love poets," there were, it must be admitted, grovelling and base-mind imitators: but any one may see how they were regarded by the true lovers, that is, the lovers of Truth, by studying the "Advertisements from Parnassus," by Boccacini, a work itself, by the way, written in a secret vein and full of sound wisdom. (See the 14th Adver., of the 2d century). The Masonic society, claims I believe, to be at least as old as the days of Solomon, and why should it be considered strange, that a class of men should exist, who regard all conflict in the world as proceeding from those who occupy a lower stand-point than reason aims at, and who seek peace by a veil which is such only to those who happen not to take their point of view.

"Alas! alas! away and end for me  
These fights of tyranny and slavery;  
I'm tired of them, for scarce they're ended when  
From the beginning they commence again;  
And none observes that he is only banter'd  
By the Asmodeus in whom all is centered.  
For freedom's rights, they say, this war they brave!  
'Tis, when exactly viewed, SLAVE AGAINST SLAVE."

[Faust, 2d Part.]

Goethe said of his own writings, that he regarded them all as symbolic; and the beauty of his works can only truly appear, when their symbolism is penetrated. From this point of view Wilhelm Meister becomes a profound study. It ceases entirely to be the mere novel which Jeffrey reviewed, and exhibits a great and solemn picture of human life, interspersed with episodical sketches of the most remarkable individualities, one of which is the "New Melusina" in the Travels. This, the 16th chapter in Carlyle's translation, is a symbolic representation of the rise and course of a poetic genius; its start from ordinary life, (the cook and landlady;) its joyous elevating power, careering in a carriage with seemingly inexhaustible pouches of gold and silver (imagination and fancy);—its decline under the lowering influences of its employment on inferior subjects;—the doubts raised about the wisdom of obeying its impulses, and the re-assurances under a decision to employ it under the guidance of reason (improved by a "certain balsam");—the incompatibility of its association with moroseness and caprice:—and then is shadowed out the successive developments of "dwarfs," (imagination); "dragons," (animal passions); "giants," (intellectual passions, ambition, &c.); and finally, the "knights," (reason): and then we see how the author has contrived to "marry" a knight and a dwarf from time to time, as in Shakespeare, and in the author himself. The whole thing is filled with characteristic touches; the improvidence of the poetic temperament, commencing a journey with "extra post, and fronting the end on foot;"—its aversion to "ants," industry; the loss of its (the imagination's) "twin brother," truth; its opposition to mere mechanical views of life and of nature, "music makers"; and its never doing anything in the "right-handed way." Finally, the imagination sets its subject down where it was taken up, in common life, "with the cook and the landlady."

In this same volume of Meister's Travels, the whole of which is symbolical, the "miners," at the opening, are *students*, seekers after truth, represented as *rocks*, (principles) of older or newer formation, or more or less universality;—and so, "mountains," in the letter of Wilhelm to Natalia, chapter 1st, are sciences or knowledges, which make a "stronger separation" among men than geographical distances. This style of writing was ingrained in Goethe. But he makes Wilhelm object to Jarno's finding satisfaction by hunting among "rocks and stones," though Carlyle has omitted a portion of this from chapter five, most unaccountably, for it beautifully illustrates Goethe's opinions upon this mode of writing, and is the best defence that can be made of it. The French translator of

Meister has preserved the suppressed passage, as follows: (in continuation of Carlyle's fifth chapter of the *Travels*, where Meister finds Montan,—Jarno, under a new name, indicating a change of views—hunting among the rocks, and addresses him:)

—“Il n'est pas dans ta nature d'aimer les choses que tu ne saurais comprendre. Sois franc, mon ami; dis-moi d'où te vient ton subit amour pour ces pierres froides et insensibles?”

—Voilà ce qui serait fort difficile à dire de toute espèce d'amour répondit Moutan.

Et après un instant de silence il ajouta:

— Les lettres sont sans doute une belle invention; mais elles sont insuffisantes pour exprimer les sons; et les sons, si indispensables à toute communication, ne rendent pas encore tout ce que nous éprouvons. Aussi finissons-nous par nous contenter des lettres et des sons, sans être pour cela plus avancés que nous ne le serions si nous n'avions ni les unes ni les autres; car nous ne parvenons jamais qu'à nous communiquer la partie la plus vulgaire des sensations, celle enfin qui ne vaut pas le peine d'être transmise.

— Tu éludes la question, mon cher; comment appliquer tes singulières paroles aux pierres et aux rochers?

— Et si ces pierres et ces rochers étaient pour moi des lettres que je cherche à déchiffrer pour composer avec elles des mots et des phrases, pourrais-tu m'en bâlmer?

— Non, sans doute; mais je dirais que tu as choisi un alphabet bien compliqué.

— Pas tant que tu le penses: la nature n'a qu'une seule écriture; et quand on est parvenu à la lire couramment, on ne s'expose jamais à s'entendre dire, par quelque critique sincère, que ce document est apocryphe, ainsi que cela nous arrive si souvent avec l'écriture des hommes sur les vieux parchemins, que nous nous donnons tant de peine à déchiffrer.

— Cela n'empêchera personne de critiquer tes nouvelles occupations.

— Je le sais, et je m'en inquiète fort peu. Quant à toi, je t'aime trop pour ne pas dédaigner entre nous le misérable échange de paroles trompeuses ou vides de sens.”

But I am travelling away from the Hermetic philosophy, though for the purpose of illustrating to some extent their mode of presenting their doctrines. I am not explaining the doctrines themselves, for I have not yet fully discovered them, and for this reason, as I have already said, I am in no danger of disclosing their secrets. I only



say what their object was not, simply adding, that the subject of their Stone is Man, and that the "divine science" aims at the perfection of man; I do not undertake to say how this is to be obtained, though something like a verbal definition of it, derived from others, may be stated without much difficulty.

To understand these writers, I am convinced that a certain experience is necessary, in which nature acts in and upon man under a sense of striving after the truth; be this what it may, the striving itself being nature in us, and the truth attained being also nature. The perfection of man it is said, lies in a certain union (I do not explain it) with God; or, in "a knowledge of the union of the soul with the whole of nature" by which the soul reaches a certain "*acquiescentia in se*," which no mere worldly event can affect, because it reposes upon the immoveable. In reality however, this union is already an eternal truth, for man has no existence independent of God, "in whom he lives, moves, and has his being," as St. Paul tells us. Here is one of those seeming contradictions, which no art of language can evade, to wit;—that man is required to attain a state, the existence of which is already affirmed, namely:—his unity with the divine nature. To set down in words something of this mode of looking at things, admitting the imperfection of the statement, I would say, that a certain one is first conceived (and let it be remembered that an intellectual conception, or idea, has a working power); a certain all-embracing unity, which Plato calls *one and many*, (expressly repudiating the notion of one being many, or many being one); one substance (according to Swedenborg); one essence; one existence; that which some of the neo-platonists called "the alone" &c., which no Hermetic philosopher pretends to *name*, because a name indicates some particular thing;—but God is not a *thing*. But though not specifically named, as man is named, or as "his ox or his ass or anything that is his" is named, yet a multitude of words set out this one, if not us he is in himself, which human conception may not attain to, yet in so far as he is manifested, or made known in his works, where alone he is seen or recognized; but the Alchemists set this forth symbolically, as by the "philosopher's fire," or, as "aqua philosophorum;" a "water that wets not the hand;" or, as a "fire which warms without burning" &c., &c.: It is sometimes called the stone, as the macrocosm, while the microcosm, is no less called the stone; and it is called *argent vive* and a thousand other names, which are employed sometimes in an eminent, but often in an inferior sense, to be discovered only by a close study of the connection in which the words are used. Now, man is supposed to come

from this *one*, and the problem is, his return to it, or to a knowledge of his union with it, though in reality he is never out of it. Let the contradiction appear what it may, man is regarded as a mineral; first in a rude imperfect state, like mineral ore before being perfected by art. He is treated not as *one*, but as if he were a composite of two things, both of which may be called attributes of the *one*, to wit:—soul and body, or mind and matter, symbolized by sulphur and mercury. One writer rather fantastically, it would seem, uses one word, sulphur, and divides it into two *sul* (for spirit), and *phur* (for body); which I mention because the author, much talked about but little understood, has been so much ridiculed for his nonsense; but the nonsense lies in not seeing the sense of it, or, at least, in not seeing the aim of it. The two are also called sol and luna; male and female; superior and inferior; brother and sister; form and matter; osiris and isis; oromanes and arimanes, and hundreds of other names, whose signification must not be taken from any lexicon, but must be sought in the nature of things; for, what cannot be found there will not be found anywhere. Now, the spirit (argent vive, salt, tartar, alcahest, hileg, flogiston, &c., &c.,) is in the stone (man): in the soul and also in body; not as it is infinite; but, in so far as it is expressed, set forth, developed, or exhibited in a partial mode by the soul and also by the body. But each of these exhibits the *one*, not according to the nature of the *one*, but according to its own nature, so long as the man is in his primitive or rude state, or, while in the condition described by St. Paul as the natural man; (for, indeed, the Hermetic doctrine, so far as I am able to interpret it, is entirely “at one” with christianity, though not in any sectarian sense, for the authors seem equally to have abjured all controversy and all spirit of proselytism.) The sulphur and mercury, as such, do not exhibit a unity; but, on the contrary are at feud with each other; though, in fact, they are one in substance; and before the unity can appear (though already there) the hard natural state must be softened (the stone must be “calcined”); that is, the man must be made to yield up his selfishness and conceit, and become as a “little child,” willing to learn, and to be absolutely controlled and guided by the Spirit of God. This state is one of transition and is represented as a great struggle;—as a violent conflict with a dragon; and as this is often brought about through trials and sufferings, until “the foul crimes done in the body are burnt away,” it is called the “black state:” and is deemed to be highly promising as being the commencement of the “perfect work:”—on the principle, perhaps, that no man will set very earnestly about im-

provement until he is made sensible of the need of it. When this black state has sufficiently softened and subdued the stone, that is, has brought the man to a state of repentance, "not to be repented of" (Hierocles)—and brought its two elements into such a homogeneity that "the spirit can enter the body and the body become spiritualized," preparatory to a union, the *white* state of the stone is supposed to be entered upon; and this is called the *second* of the three "operations," though all three operations are in some sense but one.—For, says Roger Bacon, "the knowledge of this art consisteth not in the multiplicity, or great number of things; our stone is but one, the matter is one, and the vessel is one: the government is one, and the disposition is one. The whole art and work thereof is one, and begins in one manner, and in one manner it is finished." Another writer expresses himself in this, quite open manner;—"some calumniate and scandalize this serious and divine work, as a fictitious thing, and they are such, whose easy confidence (forgetting the *cautions* of the philosophers) believe all true as they find it written: And when after tedious and expensive chymical operations, (the expressions of the philosophers *seemingly* to look that way) they find no reality in the experiments, then, in a discontented humor (perhaps having been cheated to boot) ruin and destroy all they have before undertaken. But it is no wonder, if they be at much expense that make use of many things: what need is there of so vain a use of many glasses, so much blowing of the coals, such consumption of fire, and other impertinent and expensive preparations: when the philosophers tell us, *one glass, one furnace, one FIRE* (and that an immaterial one, not to be found in the furnace of the chymist) is sufficient to perfect the work;—which, whosoever attempts, and cannot first perceive that the work is to be gone through without charge (at least very little or inconsiderable) let them leave off, and desist; lest the consumption of their wealth leave their hearts as cold, as the drudging in a false fire hath made their faces pale." This same writer adds: "by way of caution, therefore, beware of those mercenary pretenders that (boasting much of their abilities) offer to discover to you any of those secrets, upon condition that you give them such or such a sum of money; for by this tinkling sound you may judge them counterfeit metal. Never was this Holy Secret communicated to so wicked a man as would or durst make *sale* of it; nor indeed do such men stand in need. They want not money, and are under no necessity to condition for a trifle who possess so great and inexhaustible a treasure; *for length of days is in her right hand, and in her left hand riches and honor.* Therefore he who hath



this, hath all; it encircling within itself all temporal felicity, health of body and all good fortune."

I cannot help remarking here the strangeness of the fact, that such passages should not have opened the eyes of more readers to the true object of the Alchymists, especially as they are of continual recurrence in almost all of their works; for although they have written with the most studied obscurity they are constantly warning us of that fact, and cautioning us not to take them literally.

But I must return to the white state, in which the stone is capable of receiving another color and so becoming "rubified." This white state is entered upon when the man (the stone), truly forsaking all selfish ends and sincerely anxious for the truth, for its own sake only, and not for any imaginary profit attending its possession, surrenders himself, soul and body, to divine influences, &c. This white state is considered intermediate between the black and the red state, this last being the perfection of the stone. Now the white and the red state are said "not to differ in essence;" for when the truth itself, and that alone is desired, free from all "by respects," it becomes prolific of all sorts of excellence. Through this a return to God is effected, for God is truth. But he is no less wisdom, power, goodness, perfection, blessedness &c., &c., and thus the regenerated man enters into the "joy of his Lord," and becomes blessed beyond all the blessings which earth can give, and his blessings are such as earth cannot take away.

As the passage to this experience is infinitely various, the philosophers, the title by which they generally refer to each other, have varied their modes of exhibiting it. Yet there is, nevertheless, an extraordinary unanimity among the genuine Alchymists who understood the true object of the "divine science;" but it must be admitted that there have been others, and there may be, at this time, for aught I know, others who, mistaking the real object, have wasted their lives and consumed their wealth in the vain search after some metal of transmuting powers by which ordinary metals might be turned into gold. Such men cannot accuse the philosophers of having misled them; for they were led away only by their own natural desires, tastes, and tendencies. Naturally selfish men will only serve God on condition of going to heaven, but no man ever reached heaven on a contract of this sort; and such men can never have any sympathy with the object of the Alchymists, but will hold their "science" and their modes of discussing it in contempt; while the philosophers truly such, "abdicate life and find themselves contained in it," not upon a calcu-

lation of profit, but by some process which I neither have revealed nor can reveal. So far as they can be said to *seek* anything, it is the condition "shadowed" forth by a pretty little poem of the 16th century by Heriot de la Borderie, translated by Cary.

"There is an isle

Full as they say, of good things; fruits and trees  
And pleasant verdure: a very master-piece  
Of natures; where the men immortally  
Live, following all delights and pleasures. There  
Is not, nor ever hath been, Winter's cold  
Or Summer's heat; the season still the same;  
One gracious Spring, where all, e'en those worse used  
By fortune, are content. Earth willingly  
Pours out her blessing: the words "thine" and "mine"  
Are not known 'mongst them: all is common, free  
From pain and jealous grudging. Reason rules,  
Not fantasy: Every one knows well  
What he would ask of other; every one  
What to command: thus every one hath that  
Which he doth ask; what is commanded, does.  
This Island hath the name of Fortunate:  
And, as they tell, is governed by a Queen  
Well spoken and discreet, and therewithal  
So beautiful, that, with one single beam  
Of her great beauty, all the country round  
Is rendered shining. When she sees arrive  
(As there are many so exceeding curious  
They have no fear of danger 'fore their eyes)  
Those who come suing to her, and aspire  
After the happiness which she to each  
Doth promise in her city, she doth make  
The strangers come together; and forthwith,  
Ere she consenteth to retain them there,  
Sends for a certain season all to sleep.  
When they have slept so much as there is need,  
Then wake they them again: and summon them  
Into her presence. There avails them not  
Excuse or caution; speech however bland,  
Or importunity of cries. Each bears  
That on his forehead written visibly,  
Whereof he hath been dreaming. They whose dreams  
Have been of birds and hounds, are straight dismissed;  
And at her royal mandate led away,  
To dwell thenceforward with such beasts as these.  
He who hath dreamed of scones broken, war,  
And turmoils, and seditions, glory won,  
And highest feats achieved, is, in like guise,  
An exile from her court, whilst one whose brow  
Is pale, and dead, and withered, showing care  
Of pelf and riches, she no less denies  
To be his Queen and Mistress. None, in brief,

Reserves she of the dreamers in her isle,  
 Save him, that, when awakened, he returns,  
 Betrayeth tokens that, of her rare beauty  
 His dreams have been. So great delight hath she  
 In being and in seeming beautiful,  
 Such dreamer is right welcome to her isle.

All this is held a fable: but who first  
 Made and recited it, hath, in this fable,  
 Shadowed a truth."

There is no violence to either truth or language in saying that the Hermetic philosophy (or the alchymical pursuit of the Philosopher's Stone) is in perfect harmony with the christian religion, especially so far as what is called the new birth makes a central point of belief with a christian. The declaration, that, "except ye be born again ye shall in no wise see the Kingdom of God," might have been taken as a motto by every Hermetic writer, from the earliest period to the present time; for the whole scope of the "science" is to indicate or *produce* a birth of or in the spirit. The two principles of soul and body (sulphur and mercury, or gold and mercury, or whatever they may called), are supposed to be at war with each other (Romans 7, 23.) and the point is to show that these, as subordinate principles, must overcome and subdue each other in some way, (I do not say how), when they are in condition to embrace each other and become transmuted into the spirit—that is, "become another thing," as Bacon expresses it. The birth of this spirit is the "new birth," and when properly effected, the man is saved, casting off the old man and putting on the new. But the process is subject to infinite miscarriages, and "not every one who cries Lord, Lord, shall enter into the kingdom of heaven;" and, in general, it may be said that those who only hope to reach there have not yet entered. The mistakes on this subject are all but infinite: and the difficulty of reaching the truth must indeed be great, else "how should it be missed by almost all."

These writers insist much upon the necessity of dark and enigmatical discourses in order "to deceive the ignorant, the unwary and the profane;" but I find this no where well expressed, for the object of the enigmatical style, most assuredly, is not to deceive any one, but to avoid misleading the thoughtless and unwary, who are too much disposed to jump at hasty conclusions and fancy themselves enlightened when they do not comprehend even the difficulties of the subject; and they often rush into a violent contempt of what on a plain statement seems exposed to incongruities, not seeing that these



appearances may be entirely due to their own want of experience and insight, or the insufficiency of language in treating the subjects handled by the Hermetic writers, who therefore endeavour to indicate their opinions, and not openly express them, intending that the student shall bring a key in his own experience and observation. The maxim of Lord Bacon is altogether applicable here, that "books teach not their own use:—this is an art beyond them, won by observation."

The careless, the thoughtless, the profane, are not likely to be led away by reading of salt, sulphur, and mercury; while the prudent, the ingenious, the well disposed, may find something to reflect upon in books which the more they are studied the more they will indicate that a permanent light is in the world: and this, to be seen, perhaps, needs but little more than that man should turn towards and acknowledge it instead of turning his back upon it, denying it.

The test of all writings must, under God, be what is called nature; but what nature is in itself, no book can tell. As I have already said, if a picture, a portrait, be exhibited, every one pronounces upon its likeness, but no one judges by the picture itself, but by what he knows of the original: and so of great nature; whosoever undertakes to represent it or its operations, by books or by paintings, or in any other manner, must be judged by nature, and not by the books or the paintings. We may know that, regarding nature as the work of a perfect being, it cannot belie its author; and the only point with man is, that he understand it aright; for if he misunderstands it, it may be, or perhaps it *must* be right that he experience some evil consequence; for evil is an instrument within nature, "not to destroy but to preserve" (Plato). It indicates the limitation of a finite being whose nature would not remain (in the race) what it is, if its obstacles yielded or gave way to it; much as, if the banks of a river did not oppose the pressure of the river to go beyond itself, the river would disappear. Evil is the name of that which obstructs us in the path in which we wish to move, whether morally or physically, and disappears when the will of man is in unison with the will of God; and hence comes the importance of a knowledge of the will of God, in order to a perfect acquiescence in it. What this will is, and how a knowledge of it is to be obtained, may be called the Philosopher's Stone, for in this knowledge is involved the new birth, which, also, is true wisdom, "more precious than rubies, and all the things that may be desired are not to be compared to it."

My few last words appear to be more numerous than my first. I

am not however writing a book, but, in a miscellaneous way setting down a few impressions, not in defence of the Alchymists, but to show that they do not deserve *all* of the contempt that has been heaped upon their name and supposed pursuits. I do not design to justify either their philosophy or their mode of presenting it before the world;—certainly not their philosophy, which, as I have again and again said, I do not understand, while, as to their obscure and hidden style of writing, I am not disposed altogether either to admit or reject their reasons for it, though I confess I incline to the former, considering the state of the world when they chiefly wrote. Their style it must be admitted, affords an extraordinary protection against controversy, for if a man says, right out, that three are one, he may be met by the direct question, how *can* three *things* be one *thing*? but by talking of three somethings under the words sal, sulphur and mercury, and showing that neither of these is precisely what it appears or is imagined to be, but something else, and that that something else is not anything absolutely distinct from the three somethings, but is somehow, or in some way, or by some means to be regarded as contained in the three, “impartibly,” as the translator of Plato, Thomas Taylor, would say, why, in such a case, the student may finally come to the conclusion that, after all, he knows very little about the subject; and has as little reason to deny as to affirm anything; and then there is some chance of his learning something! But so long as a man feels certain that three things, can, by no possibility, be so disposed as to appear to be one thing, it is almost hopeless to talk with him about the mystery of the trinity; for although he may eat one and drink another and evaporate the third out of sight, he will be apt still to think of them as three *things* and not as one. The great obstacle to true knowledge is not precisely ignorance, but it is false knowledge, or an opinion that we already know, when we are in “the greatest ignorance” (Plato), and to meet this condition directly is to invite opposition, but by talking, seemingly about something else, a man may be led, step by step, into such a state that he must deny his own rationality or admit doctrines which, at the commencement of the inquiry, appeared manifestly absurd, contradictory and impossible.

I wish to add here that I am merely supposing a case, and do not intend to say that the Alchymists were technically speaking trinitarians, although I think they would not deny it, if allowed an opportunity of explaining themselves; but the explanation would still be in their jargon about mercury, sulphur, &c., ending with a recipe, which to the eye might be altogether hieroglyphical, as thus: “Our Tincture

then, is only generated out of the mercury of the wife, which is called the *Prima Materia*, *Aqua permanens*, *Acetum philosophorum*, *Lac virginis*, *Mercurius corporalis*, with which nothing extraneous, alien, or foreign is commixed, such as are salts, alums, and vitriols. Because, from this mercury alone, the virtue and power of this our magistry is generated: and it resolves every (mataline) Body, that it may be augmented or multiplied. This, our aforesaid Mercury," [I ought to note that the Alchymists sometimes write of mercury what in other places they say of sulphur, and of sulphur what they say of argent vive, &c. &c. so that one must not depend upon their words merely, but upon the properties, qualities and natures of the things spoken of.] "This, our aforesaid mercury, is both the root and the tree, from whence many and almost infinite branches spring and increase. The first work for the making of this Elixir," [he has just called it Tincture and it is Roger Bacon who is speaking] "is sublimation, which is nothing else, but the subtilization of the matter of our Stone, by which it is cleansed from all its superflisties." [I would here refer the reader to Ephes. iv. 21 to 25, and then proceed.] "The fixed and volatile parts are not separated one from another, but they remain united, and are fixed together, till they both may have an easy fusion together, in the fire." [This is not a material fire of which Roger speaks.]

"Take therefore our aforesaid *mercury*, which, in a sealed glass, put into its hot bed, for one whole philosophic month, which is forty days, till it begins in its own body to putrify and be coagulated, and all its humidity be consumed in itself, and also converted into a black earth.

"In this sublimation is completed the true separation of the four elements. Because the cold and watery elements are changed into a hot and dry earth, which is the head of the crow, the mother of the remaining elements.

"Thus our work is nothing else but a transmutation of nature, and a conversion of its elements. The spiritual is made corporeal, the liquid is made thick, and the water is made fire. Moreover the black earth is imbibed with its own water, and dried until it is sufficiently cleansed and brought to whiteness. Which then is called the *white earth* foliated, *sulphur* of nitre, *sulphur* of magnesia: and then there is a new conjunction of *sol* and *luna*, and a resurrection of the Dead Body.

"When our earth bearing fruit is moistened with its own proper



water, it drinks it up with a greedy thirst, till it generates or is made pregnant, and then brings forth fruit an hundred fold.

"Now proceed farther with the white earth, augmenting or increasing the fire to it, till by the motion of the continual heat, it is digested and brought into the highest and most pure red. And now it is called our red coral, red sulphur, blood, our purple gold, our burnt crocus.

"This very work repeat three or four times with new materials, and you shall have the most perfect red stone of the philosophers, red as blood itself, with which you may *tinge mercury*, and all other imperfect metals.

"But it behooves you to take of our aforesaid *sulphur* three parts, adding one part of fine gold, reduced into a subtle calx, and of the water thereof two parts; these three mix subtilly, till they become one inseparable matter: these then digest in a proper furnace, till they become a red stone."

After the remarks I have made, imperfect as they are, who can fail to see in this extract, which is the concluding chapter of Bacon's work, and is copied here as a sample, that Alchymy does not deal with vulgar metals, which is the main point I wish to insist upon; and, secondly, I wish to shew that man is the subject of the science, while his perfection, as much as may be, is the object of the science. The *modus operandi* I have not explained, nor do I hold myself in any manner responsible for it. Abuse it who will, they have my full leave; but I would hint that the tempers and dispositions of men are infinitely various, and if a few men in confessedly dark times found their amusement and, perhaps, security and peace, in writing about calcination, putrefaction, pulverization, submersion, decomposition, rectification, purification, separation, digestion, distillation, fermentation, liquefaction, sublimation, imbibition, composition, ceration, inspissation, descension, solution, coagulation, conjunction, commixtion, conversion, and a multitude of other words, ending with rubification; and, while occupied with this amusement, interfered in no manner with the methods of other people, who shall blame them? Would it not be wiser to look a little into what they were about, and try to discover the point of view which gave its charm to their singular employment? for some such point of view must be presumed, else how could such a man as Roger Bacon have been an Alchymist?—not that I would use his name and authority to revive what is supposed to be a died out science; but, as a point of historical interest, to look into the past intelligently, and not under a dogmatic condemnation of a subject about which we have no knowledge. This condemnation is

always uttered with a peculiar self-complacence, and a consciousness of superiority, so elevated as to exclude all sense of compassion for the "poor deluded" Alchymist. But in my judgment there never has been a class of men in the world so little needing pity and compassion as these same philosophical stone seekers; and while man remains man, in this vale, which I am careful not to call a vale of tears, for this would be a reflection upon God who made it, the aim, object or pursuit of the Alchymist must be of the first importance, whether the stone ever be discovered or not. The command is, "seek first the kingdom of God;" and he who gave this command, gave another,— "Be perfect as your father in heaven is perfect;" and another, "behold the kingdom of Heaven is within you;" and at the very time when he said that he was one with the Father, he prayed for his followers that they all might be one; "as thou, Father, art in me, and I in thee, that they also may be one in us," (John, 17th chapter.) When these several passages from Scripture shall be combined into one and become actual in the life of any one man, that man will doubtless know what the philosopher's stone is; and if he could teach the world what it is, and how to attain it, what greater benefit could he confer?

I do not know how far I may go without incurring the penalty invoked upon those who betray the secrets of this science. I have, indeed, felt very little apprehension, from the simple fact, that I am not sufficiently in possession of the science to disclose any of its mysteries; but I suppose I may say with safety, that as one man cannot see for another, so neither can he think for another; and much less can one man be saved for another. If men could express themselves in language with clearness it would doubtless be a great help in communicating ideas, for the learner might at least recognize by the sign what was intended to be signified; but this is hardly possible, in regard even to external physical things, and how then can language be implicitly relied upon when it deals with things out of sight? Plato has made Socrates say to Phædrus:—"He who thinks to leave an art in writing, and again, he who receives a writing as if something clear and solid would result from it, must be full of simplicity, and in reality ignorant of the prophecy of Ammon, since he thinks that written words are of further value than to remind one who already knows the subject of which the writings treat.

"For writing, indeed, Phædrus, has this inconvenience, and truly resembles painting. For its productions stand out as if they were alive, but, if you ask them any question, they observe a solemn silence. And so it is with written discourses; you would think that

they spoke as though they possessed some wisdom, but if you ask them about anything they say, from a desire to understand it, they give only one and the self same answer. And when it is once written, every discourse is tossed about everywhere, equally among those who understand it, and among those whom it in no wise concerns, and it knows not to whom it ought to speak, and to whom not. And when it is ill-treated and unjustly reviled, it always needs its father to help it; for of itself, it can neither defend nor help itself."

But it will be asked, why should an admitted difficulty be made greater by studied obscurity? to which I would answer, that, perhaps, the difficulty is not in reality made greater, but is to some extent eluded by what is understood to be symbolic writing; and in this way:—The visible literal meaning of symbolism is often sheer nonsense, which never misleads anybody, and only furnishes matter for a certain degree of smartness to exercise itself upon in showing its absurdity, the critic proving to all the world just what the author perhaps knew a great deal better than himself; but besides this shallow view of the majority of readers, there will here and there be found one who will look behind the curtain, and such a one will dismiss all idea of a literal sense and will seek the hidden sense; but in this search he is compelled to go to the source whence the author himself drew his materials, that is, to nature; and now his discoveries will be measurably his own, and will rise up before him with a certificate of their own. But if an author has not himself understood nature, his symbolism, not representing the truth, will simply make no impression or must pass for the absurdity visible on its face. The error of a misinterpretation must always be partial and is not likely to extend itself; and even where this occurs it must be regarded, not as the legitimate fruit of the symbolic writing, but of the incapacity of the reader, which cannot always be guarded against. There will never be wanting Wagners in the world, before whom the intelligence of Faust will be a mystery. If some men, misled by the language of the Alchemists, have really labored to make gold by an unlawful or impossible process,—I do not, in the first place, see so very great an evil in this, but I insist, chiefly, that it was their own fault. Their innate tendencies led them to seek for worldly wealth, when they should have been in pursuit of the bread of life, and while the worldly spirit dwelt within them, they were not subjects for the science of Alchemy to act upon. To realize the worth and excellence of the science, it must, like an art, be sought for itself and for nothing else; not even, if possible, for its own great reward;—and every genuine



religious spirit understands this perfectly well, when his duty to God is the question, (Matthew 5, 46). Every truly religious heart knows and feels that its "joy in the Lord" is a pure grace, and to such a mind the idea of serving God for the sake of its rewards, is an abomination. Religious minds, on the contrary, are painfully depressed when such thoughts intrude upon them, as they sometimes will against every effort to shut them out, and they often resort to self-abasement and humiliation to banish them; for they desire to devote themselves to God's service under all circumstances and conditions, and to accept, if need be, with equal thankfulness his chastisements and his blessings. I know very well I am writing the truth, without claiming to share it, and if it is not recognized as such, it can only be by those who have something to learn on this subject; and if this little tract has the effect to make any one man "think on these things," it will have done some good.

"A wise man will hear and will increase learning; and a man of understanding shall attain unto wise counsels; [so as] to understand a proverb, and the interpretation; the words of the wise and their dark sayings."

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Although, in writing this little tract, or whatever it may be called, I have once or twice thought I had said as much as is proper for one so little acquainted with the subject as myself, yet I am disposed still to add something, more especially for those, if any, who may think it worth while to look into Alchymical books. I wish to warn them that at first, there will appear to be nothing in these volumes but confusion worse confounded! There will seem to be no order or reason in anything put forth by them. Needless repetitions will apparently be observed; but that which will puzzle the student more than all the rest, may perhaps be the use of the same word for many different things; and an attempt will be perceived to make distinctions, where no differences can at first be observed:—among the latter I would point out what the writers say of *the Stone of the Philosophers*, and, of *the Philosopher's Stone*; distinguishing in like manner *Argent vive* from what is called *Vive argent*, &c., and would remark, that by these expressions the Alchymists mean merely a different state or condition of the same thing. But the cloud will tend continually to be clearing up as the student begins to seize a view of the object of the whole thing. Nature has always been said to be an enigma, and the writings of philosophers are but a part of nature, and cannot, of themselves, make that clear which is not so to the natural man, (the stone of the

philosopher,) but writings may so excite the natural man, as to bring that out of him which, in an immature state, lies buried like a light under a bushel; and then, as it tends to become the Philosopher's Stone, it sees more and more clearly, order and light, both in nature itself (always under God understood) and in what is written about it. The principle which expresses this, until the *idea* begins to work itself clear, has scarcely any meaning at all, and is mere "sound signifying nothing"—to wit; that "nature is whole everywhere," and such like expressions. The unity of nature is at first a meaningless dogma, and to most men carries no life with it; but in reality it is the "Song" (the Harmony) set forth, in the 10th chapter of Meister's Travels (Carlyle's translation), as "the first step in education; all the rest are connected with it, and attained by means of it. The simplest enjoyment, (the teacher proceeds to say), as well as the simplest instruction, we enliven and impress by *song*," &c. meaning an idea of the universal harmony; beyond all question, that which Pythagoras intended, by the "music of the spheres." So long as a man is not in harmony with himself, but carries within his bosom any special delusion or falsehood, it is not likely that he will hear, or with pleasure will hear of, the music of the spheres; to enjoy which it seems to be necessary that one's special and individual nature should nearly if not totally be denied, wherein may be seen the truth of the declaration that he who will save his life shall lose it; for the individual natural life is, in some respects, much like any other natural thing, which its possessor struggles to hold, somewhat as a man struggles to hold a worldly fortune; and it is not until after he ceases to struggle and acknowledges his inability to hold it, that he finds that he *himself* remains, an eternal mysterious existence in the whole, which he cannot only hold, but cannot but hold; for the eternal life is imperishable.

This self-abnegation is not within the power of the natural will. How then is it to be obtained, even if desired? This is undoubtedly one of the mysteries of life. Do the Alchymists explain it? Whether they do or not can only be seen by a study of their writings, whereof I undertake to say so much as this, that those authors have fully understood the nature of the questions about which so many reputed philosophers have puzzled their own and other's brains, endeavouring to explain "free-will, fixed fate, foreknowledge absolute," &c., some of whom have labored to "bridge over" the abyss between the finite and the infinite, as they somewhat ostentatiously call it. The Alchymists, as I consider, have taken a stand aside from all these controversies, having at the same time a full knowledge of their nature, and

some knowledge beyond it. It is not to be denied that many men have written extensively upon a variety of questions touching the deepest interests of man, and that, too, with perfect sincerity and a worthy purpose, when a little more light would have made them silent; and perhaps one of the most interesting discoveries that any one can make in this direction, is, that there have been men in the world more ingenious than many who "stand recorded in the book of fame:" men who in their self-sought obscurity have escaped the concealed irony involved in a spurious fame, even though some of them have had their reputations crucified by a deluded public; of which, however, no Alchymist can complain, since his reputation was a foreseen result, willingly encountered. His happiness, it would seem, has not at all depended upon popular fame, which he compared to the "moving of the waters."

I have hesitated some moments as to whether I shall be so presumptuous as to add—but my conviction is strong—that the Alchymists will be honored in the world when Kant and all his tribe shall be forgotten; and yet, to atone somewhat for this enormous heresy, I will add, that the study of Kant may be of great assistance in this very study; as no man knows the extent of his powers until after he has tried them, and found them wanting; for, as the German poet has said,—“No man is born to solve the problem of the universe, but he must make the attempt in order to know how to restrain himself within the limits of the comprehensible.”

In seeking knowledge it is of importance to understand that there are different kinds of knowledge—to be acquired, not all of them in the same way. Swedenborg, taking the hint, I must think, from one whom he did not deign (or dare?) to quote, sets forth three, which may, in brief, be called, 1st, knowledge by intuition; 2d, knowledge by reasoning, and 3rd, knowledge by the senses; not that these do not insensibly, in many men, coexist or run into each other. The greatest difficulty lies in understanding what is meant by intuition, or intuitive knowledge, because this kind of knowledge, as Plato tells us, (7th Letter,) “cannot be taught like other knowledges.” We can learn and treasure up in the memory, knowledge of history, geography and other external things; but of intuitions an external account gives no adequate idea, and the attempt to grasp this sort of knowledge by what may be called an outward effort, is really very much like one man attempting to see with another's eyes. The reality of this knowledge is denied by those who have no experience of it, while those who have it, think it little short of divine; and this is what some



men call *reason*, and are so loud in asserting its independence and proper supremacy over man. But in this sense, reason must not be confounded with reasoning; for reasoning is a mere process of the intellect, and cannot verify or certify itself. This process may be intellectually as clearly distinguished as the eye sees an external object in its isolation; and when so distinguished, it must be seen to be a certain *process*, resting upon data not contained within the reasoning itself, but either upon an intuition, or upon a sensuous observation, or finally, upon an undistinguished mingling of these two; which two are the extremes of knowledge. Intuition gives us the highest certainty of which we are capable, and besides being sometimes called reason is that which throws its light around an ordinary belief and transforms it into what is called faith, and is thence so commanding; and if it could always be clear no man would ever be misled by it. When reasoning is based upon a clear intuition, its results are also clear and decisive. But the senses, when not rectified, give us partial, broken, incomplete, inadequate and imperfect knowledge; and when reasoning, the process just referred to, has no better data, its results, even though the reasoning be ever so perfect, must share the uncertainty of the data: and, indeed, when the data are imperfect, the certainty of the reasoning only so much the more insures an imperfect result; for reasoning is somewhat like a river that can never rise above its source, and when that is clouded, the reasoning, or at all events, the results of it must be clouded also. Now, the reason, or the intuitions of it, are as real as external objects, and are infinitely more controlling. It is these that let the soul into a knowledge of the eternal and the unchangeable, by which the soul comes to "participate" in that which it sees and knows as something at the same time above what may be called the natural man, and yet not absolutely foreign to the whole man. Through some perception of this kind the man begins to learn the true dignity of his own nature, and understands that the soul is infinitely greater than that outward instrument of it, which mingles daily in the affairs of the external world; and when thus duly impressed with a sacred awe of himself, as a divine something, the man easily glides into what may be truly called an experience of his own immortality: for to recognize the eternal is to share it, since this can only take place in a nature capable of it:—somewhat as the sun is seen, not by a power merely in the sun, but by a power in the man who sees it; and as this power of vision exists, in its essence, (though I dislike this word) in the blind man, no less than in other men whose merely instrumental eyes are perfect, so the essential nature of man

is eternal, whether the man, "while in the body," becomes conscious of it or not.

But the immortality of the soul is something quite different from the perpetual or continued existence of the natural man, which comes into being and perishes before our eyes, like all other natural things; and he who hopes to live immortally as an unchanged natural man, has no proper idea of immortality, and assuredly comes under the judgment contained in the text just quoted from Matt. 16, 25. There is an intimation in this verse, that there is something more to be surrendered than mere external property, for it requires a man, so to say, to surrender his very self. But the natural man,—a phraseology I adopt only for its convenience,—desires to enter into life with all his natural properties and propensities, as these are apprehended through a sensuous perception of himself, not seeing that this perception itself is perishable like all it fastens upon, and would cling to as the true reality. But a conception of the truly real, involves necessarily a negation of all this; and in one word, the birth of the new man is the death of the old man, which is but one operation, however brought about, as the Alchymists are careful to represent; for, as I have repeatedly said, the doctrine of the new-birth might have been taken as a motto by every alchymical writer who has ever attempted to shadow out his opinions, by writing seemingly of *argent vive*, sulphur and mercury, or by mercury, sol and luna, or by any other of their strange terms, adopted for reasons best known to themselves.

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I did not intend to add any thing more, but while the compositor is at work, and before he catches up with me, I shall have time to remark, that the universal impression seems to be, that the Alchymists were merely in pursuit of something which as yet has never been discovered; and no one remarks, that, in all their writings, they not only manifest most decisively their sense of being in possession of the "Stone," but the very object of their books is to teach, in their way, the method by which others may discover it. Dr. Mackay says that Roger Bacon spent much time in *pursuit* of the Philosopher's Stone,—as if he had not discovered it; but if the Doctor had looked into Bacon's works on the subject, he would have seen no intimation of the slightest doubt about his being in possession of it; and it is the same with every one of the writers in this "science," whose works I have consulted; and, what is most remarkable, there is nothing like a dispute among them on the subject, but there exists the most astonishing unanimity, forming, in this respect, the greatest possible con-

trast to the habits of the "Ethnick" Philosophers, among whom each new candidate for fame commences by demolishing the theories of all his predecessors; so that philosophy, in the hands of Hobbes, Locke, Hume, Kant, Fichhe, Schelling, Hegel, &c., is a perfect saturnian monster, and permits no child to gain anything like a reasonable maturity. Not so with alchymical books: here no one book destroys another, but each helps, on the contrary, to throw light upon every other, until the serious student begins to perceive that the object aimed at being eternal, cannot be said to be directly contained in a perishable volume; and that, in fact, a book has done its office when it has put the student on the search, leaving nature to do the rest. But I would recommend the greatest possible care, not to be misled by hasty conclusions and mere suppositions as to the meaning of these writers; and here, as in other reading, it is one thing to ascertain the meaning of an author, and quite another thing to pass a judgment upon that meaning; and this is precisely the point wherein the author cannot help the reader,—for which reason, this most essential of all points is so apt to become "a stone of stumbling" to the careless and unwary. Look well, therefore, I would say, to the root of the opinions which you *imagine* you discover in Alchymical books, a necessary caution, indeed, in all sorts of reading, but particularly in books by Hermetical writers; and if you find it moveable, my advice is to lose no time in seeking a new meaning; for as in all the arts, so especially in the art of life, nature does not follow us, but requires us to follow her; or, in the language of one of my new friends:—"nature and art ought so lovingly to embrace each other, as that art may not require what nature denies, nor nature deny what may be perfected by art. For nature assenting, she demeans herself obediently to every artist, whilst by their industry she is helped, not hindered: of whose steps, progress, motion and condition, whosoever is ignorant, let him not presume to attempt this work, (of itself abstruse, and wonderfully shadowed over by philosophers with infinite clouds:) for nothing will answer his expectation, who either knows not or strives to compel nature."

While these sheets are going to press I may as well correct an error,—a slip—on page 14, where *Horus* is named as one of the Hermetic Trinity in the Egyptian fables; I should have named *Osiris*, *Isis* and *Mercury*, and not *Horus*; for in the Hermetic Theory, applied to the explanation of Egyptian fables, *Horus* represents the "philosophical stone," or the "philosopher's gold," sometimes called the "philosophic child,"—in short, the new birth; for, in this doctrine



everything clusters around this rare phenomenon, by which a man is supposed to pass from a sensitive to what may be called a spiritual life, while, yet, he remains no less a man. For the "vase" of the Alchymist is a man, in which the whole work is begun and ended, and is but one: and the so called "great work" is accomplished by means of a certain philosophic fire, which is sometimes also called water, though all expressions of this sort are used only by way of remote similitude. But what does the similitude signify? This is precisely what is not explained in the written works: but we see how the nature of fire consumes and converts everything to itself; and water—we see—by one operation passes partly into air and partly into earth, while, in itself, it is both, yet neither. These sensible exhibitions must be considered as infinitely remote shadows of what is intended to be illustrated, the truth itself being so imposing and majestic as quite to overcome and silence the student; for he feels how inadequate words are to explain what, nevertheless, seems clearer to him than the sun at noon-day;—in which new light many of the pursuits of manhood or middle life lose much of their importance, and some of them dwindle into the insignificance of hoop-rolling, the innocent amusement of childhood; while some men, it is believed, would be most happy if they could exchange their grave pursuits for the simple exercises of early life, before "vitriols" and "arsenical poisons" had corroded the pure metal of the stone, and so disfigured and defaced it, as to make it difficult to recognize the mine from whence it came.

There may appear to be some confusion in the use of words, if not of ideas, in saying in the first instance that the Philosopher's Stone is the symbol of wisdom, and afterwards assigning the perfection and also the salvation of man as the *object* of the Alchymists, and finally insisting that the "divine" science relates to the so called new birth. But a little reflection will, I hope, satisfy any one, that a wise man must also be perfect according to his nature, which perfection would be defective if it did not secure salvation; and, finally, the experience of the new birth is a culminating point in humanity, beyond which no man can pass, or desire to pass, while "in the body;" and this therefore must also be the perfection of man.

I know very well how much this doctrine is exposed to mistakes, and that it is a fruitful source of wild fanaticism; but fanaticism is to religion what smoke is to fire, and we all know that wherever there is smoke there is also fire. I have no wish to dogmatise about these matters, and nothing is further from my purpose than to set myself forward as a teacher. I understand my place better; yet I suppose I

may give a simple statement of my impressions without incurring the charge of presumption. I wish to say, then, that although the doctrine of the new birth is unquestionably a doctrine of Christianity, the experience itself is a property of human nature, and was known long before the founder of Christianity gave his sanction to it. It has often been remarked that when Christ announced this doctrine to Nicodemus, he, at the very same time rebuked him, that, being a teacher in Israel, he was ignorant of it, as if he ought to have known all about it. Many have supposed that this doctrine was taught in the Eleusinian mysteries, and at all events it is certain that the ancient Brahmins were well acquainted with it. No better evidence can be adduced for this latter fact than the Institutes of Menu, translated by Sir William Jones. In this volume the perfected Brahmin is everywhere spoken of as the *twice-born* man, and the nature of the second birth is as clearly recognized as it can be, in such passages as these, from the ancient work just named:—

“Of him who gives natural birth, and him who gives knowledge of the whole Veda, the giver of the sacred knowledge is the more venerable father; since the second or divine birth insures life to the *twice-born*, both in this world and hereafter eternally.

“Let a man consider that as a mere human birth which his parents gave him for their mutual gratification, and which he receives after lying in the womb: but that birth which his principal Teacher, who knows the whole Veda, procures for him by his divine mother the *Gayatri*, is a true birth: that birth is exempt from age and from death.”

After setting forth the unity of the divine nature, and recording the injunction, that the “Law” is to be kept from “persons unfit to receive it,”—the Institutes close with this passage:—

“Thus the man who perceives in his own soul, the Supreme soul present in all creatures, acquires equanimity towards them all, and shall be absorbed in the highest essence, even that of the Almighty himself.”

I find among some translations of Pythagorean Fragments, by Taylor, a passage attributed to Archytas, plainly, to my mind, conceived in the same spirit as that just quoted from Menu;—to wit:—“Whoever is able to reduce all kinds of things under one and the same principle, this man seems to me to have found out an excellent *specula*, or high station, from whence he may be able to take a larger view and prospect of God and of all things; and he shall clearly perceive that God is the beginning and end and middle of all things that are per-

formed according to justice and right reason." I find this same doctrine in Plato's *Sophist*. (Taylor's Ed. of Plato, vol. 3, pp. 260-1, and Bohn's Ed., vol. 3, p. 161. See also Bohn, vol. 4, pp. 524-5.) And, indeed, nothing seems better determined than that wisdom, (as distinguished from knowledge,) perfection, salvation, and the new birth, are in some manner—let those explain it who understand it better than I do—involved in a true idea of God; not a form of words expressing a current belief, and repeated by rote, but a living truth, which, when it enters the soul, works there like the "fire" of the Alchymists, consuming and destroying whatever is foreign to its nature, and the man is saved, not with his natural and habitual wishes, but by a certain transformation, or, what the Alchymists call a transmutation:—not that God is changed in any manner, but that the man is no longer what he was, but "a new creature;" and now, the man being changed, the earth itself seems transformed and becomes in some sort a New Jerusalem, accomplishing what seems to be but a dream to us in a merely natural state.

It will take a great deal to convince me that the *angels*, of whom so much is said by Swedenborg, were any other than perfected men in the sense above hinted at, though I know that this would be stoutly disputed by the Swedenborgians of the present day. But whoever studies Swedenborg closely will see everywhere exhibited the *sal*, *sulphur*, and *mercury* of the Hermetic philosophers. Let no one be startled at this, for the truth, though one in itself, may be expressed in many ways. Swedenborg cannot be readily understood by any one who is incompetent to understand his mathematical and philosophical writings, the fruit of the labor of the first half of his life; for his so called spiritual views were greatly influenced if not determined by his early studies. This may appear strange to those who do not consider that the imagination has its laws no less than the reason. I am perfectly satisfied that the best mind to bring to the comprehension of Swedenborg's writings, is a mathematical mind; a mind that knows why the three angles of a triangle are eternally equal to two right angles. How can any one presume to say he understands Swedenborg's religious views, who is incapable of comprehending his "*Principia*," a more difficult book to understand than Newton's? With Swedenborg the soul is but the life of man, while the spirit is the man himself, and the body is but an instrument; and to be let into the spiritual world, in Swedenborg's sense, is nothing but to become conscious of the spirit in a man's self, which sees what it sees out of relation to time; and this, again, is nothing else but to find the philosophic



gold, or, "the Philosopher's Stone." This is an absurd interpretation to those who read Swedenborg literally, but some people are very hard to be convinced, even of very plain truths; as, for example, the countryman, who read very diligently the whole of Gulliver's Travels, and yet, notwithstanding the air of seriousness and gravity pervading the whole work, plainly evincing the sincerity of the author, he laid it aside with the solemn declaration, that there were *some* things in it that he could not believe; by which we may see the real ground of much of the infidelity in the world, and how deeply seated it is. What must be done with such people, and how are they to be approached? I "know nothing" for this purpose equal to the contrivance of the Hermetic Philosophers, by which the members of the fraternity know each other infallibly, by right of nature, and escape the groping and contaminating controversies of all the 'rest of mankind.'

But let no one imagine that he can put on and off this doctrine as he dons and doffs his coat. (Jer. 13, 23. Matt. 7, 16.)

"The earth, that's nature's mother, is her tomb: -  
 What is her burying grave, that is her womb;  
 And from her womb children of divers kind  
 We sucking on her natural bosom find:  
 Many for many virtues excellent,  
 None but for some, and yet all different.  
 O! mickle is the powerful grace that lies  
 In herbs, plants, stones, and their true qualities:  
 For nought so vile that on the earth doth live  
 But to the earth some special good doth give;  
 Nor aught so good, but strain'd from that fair use,  
 Revolts from true birth, stumbling on abuse;  
 Virtue itself turns vice, being misapplied,  
 And vice sometime's by action dignified.  
 Within the infant rind of this small flower  
 Poison hath residence, and medicine power:  
 For this, being smelt, with that act cheers each part;  
 Being tasted, slays all senses with the heart.  
 Two such opposed kings encamp them still  
 In man as well as herbs, grace and rude will;  
 And where the worser is predominant,  
 Full soon the canker death eats up that plant."

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AND  
THE DISCOVERY  
OF THE  
CHEMICAL CONSTITUTION OF WATER.

A L E C T U R E ,  
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SESSION OF 1855-6.

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BY PROF. LEWIS H. STEINER, M.D., &c.

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To the student of any particular branch of human knowledge, one of the most interesting subjects is the history of the discovery of its principles, and the various incidents in the lives of those men who have given an impetus to its study. *Here* he can see how many difficulties had been encountered before the very basis of knowledge was attained; how many days and nights of toil were consumed in quarrying from the rough mountain the huge blocks, and in subjecting these to the ponderous blows of heavy hammers, as well as the fine strokes of delicate chisels, so that they could be used in laying the foundations and shaping the corner-stone of the superstructure, which now strikes the eye with its symmetrical form and passing beauty. He will find that each step in the progress of a science has been marked with labor of the most intense kind; that, although the results are striking and seemingly self-evident, they are no more so than the erection of some grand



architectural structure, some noble old cathedral pile, where the architect's idea has been so well carried out in every part, that the spectator is forgetful of the enormous cost, the great expenditure of money, and time, and human labor, required to develope and represent this idea. Every course of stone has been laid with care, and much fatigue has been undergone in placing it so that it shall be able to withstand the weight of those destined to be placed above it. And all depends on the foundation being securely laid, deep below the destructive influences of the frost, and on the solid clay or still more solid rock, so that no ordinary tempest or earthquake shall unsettle those walls which embody the idea that had existed in so much beauty in the architect's mind.

No study can be more instructive than an examination of the difficulties the great men of the past have experienced in their toilsome investigations. We not only learn to appreciate the importance of the latter, but we acquire a knowledge of the causes which impeded their progress, and which we should avoid in conducting similar original investigations for ourselves. Thus profit is not only directly derived in the way of knowledge gained, but indirectly also, since we learn to avoid the shoals and quicksands on which the strong barks of others have nearly been made perfect wrecks.

The history of Chemistry is full of most interesting facts connected with its great discoverers, and it is well for its students to rest awhile from their labors and to peruse these with care, so that they can estimate properly how great is the light under which they now prosecute their studies, and to whom they are indebted for it. It has been thought that some things connected with the history of Cavendish and his discovery of the chemical constitution of water might not be unprofitable or uninteresting.

Henry Cavendish was one of those few men, coming from the wealthy ranks of society, who have not only been Mæcenas to science, but who have expended their time and talents, as well as their money, in its cultivation and advancement. His name and his fortune, his intellect and his life, were freely expended in the cause of science, so that when the great French mathematician, Biot, summed up his character, he felt

that he could truly say, that Cavendish was "*le plus riche de tous les savans et probablement aussi, le plus savant de tous les riches.*"

He was the son of Lord Charles Cavendish, the third son of the second Duke of Devonshire. The family can be traced as far back as 1366, in the reign of Edward III., and it seems to be singularly marked, according to Dr. Wilson,\* "for the high moral character which for so many centuries it has maintained."

He was born at Nice, October 10, 1731; entered the University of Cambridge December 18, 1749; and left the same, without graduating, in 1753. Of his early life we know comparatively nothing, partly on account of the neglect of contemporaries to record such incidents, and partly on account of the peculiar retiring habits of the man himself, which prevented him from speaking of his early life or indeed of unfolding his inmost character even to those who knew him best. He became a member of the Royal Society in 1760, and from that time up to the period of his death, in 1810, presented many most valuable papers to this Society. We find him spoken of† as "an excellent mathematician, electrician, astronomer, meteorologist, and geologist, and a chemist equally learned and original. In the fullest sense of the term, a natural philosopher; and had he published during his lifetime all the researches which he completed, his reputation would have been much wider and more varied even than it was." But a natural repugnance to appearing before the public prevented him from doing that thing men are so prone to do—to announce the novelties they have discovered, or even to magnify their importance.

As a man we find nothing in his character to love—a stern, impassive representative of a cultivator of science and nothing else. His biographer describes him‡ as one "who did not love; he did not hate; he did not hope; he did not fear; he did not worship as others do. There was nothing earnest, enthusiastic, heroic, or chivalrous in his nature, and as little

\* Life of Cavendish, p. 14.

† Life of Cavendish, p. 19.

‡ Life of Cavendish, p. 185.

was there anything mean, grovelling, or ignoble. \* \* \* \*  
 An intellectual head thinking, a pair of wonderfully acute eyes observing, and a pair of very skilful hands experimenting or recording, are all that I realize in reading his memorials. His brain seems to have been but a calculating engine ; his eyes inlets of vision, not fountains of tears ; his hands instruments of manipulation which never trembled with emotion, or were clasped together in adoration, thanksgiving, or despair ; his heart only an anatomical organ, necessary for the circulation of the blood."

It may be fairly asked, why bring such a character forward for examination? Surely it is not desirable that it should be imitated? Are we not created for grander and nobler purposes than to be mere negations in a world where one's social influence is of such immense importance? Is it enough *not* to be a villain, a debauchee, a murderer? Or, rather, is it not our duty to be *something* that shall create an influence for *positive good* on our fellow-men? To this the answer must be made, that the character of Cavendish is not introduced as a subject of admiration, or for imitation, but rather as a warning to all men who cultivate the intellect, that they do not neglect the social portion of their nature. While they are rising higher and higher into those regions where an almost intuitive power is given them of perceiving the secrets of nature, it is necessary to strengthen the links of that chain which binds man to man, and which become brighter and brighter with each deed of love and philanthropic kindness. The character of Cavendish thus may serve as a warning set up in the highway of science, to let men beware of immolating all that is common with their fellow-men on its altar, although the investigations they may prosecute shall eventuate in much general good. Their duties are more extensive. *as men*, and while students of science they must not forget these, else we shall class them as Cavendish was classed, as "a cold, clear intelligence, raying down pure white light, which brightened everything on which it fell, but warmed nothing," just as the cold moon may light the traveller's path across the trackless snows, but not contribute one genial ray of heat which shall enervate his strength, contribute to his comfort, or help him to withstand the icy blasts that are so furiously beating against him.



A word as to the subjects which claimed attention from Cavendish's clear mind, and the general nature of his contributions towards their full elucidation, and we shall proceed to the special discovery we wish to examine at this time.

The determination of the specific gravity of the earth occupied his attention for a long time. His determination (A. D. 1798) was 5.4; and although many experimenters have repeated *his* experiments and made others with reference to the same subject, this number has not been materially altered, the decimal only having been found incorrect, and the specific gravity now being considered 5.6. He determined the freezing point of mercury as between  $39^{\circ}$  and  $40^{\circ}$  Farenheit, by a series of experiments which were performed, (A. D. 1782,) in accordance with his directions, by Governor Hutchins, at Albany Fort, Hudson's Bay. Prior to this, it had been considered by Braun at between  $300^{\circ}$  and  $400^{\circ}$  Fahrenheit; and the most singularly discrepant views were entertained as to the exact point. The consideration of many subjects connected with heat is so closely bound up with a proper knowledge of *this* point, that its importance will be at once recognized.

Next we find him making some experiments relative to the exact composition of the air; and although the two main constituents of the air were already known, yet it was left for Cavendish to show, that in any given quantity of air, the maximum of consumption of its oxygen by a burning body was one-fifth, and that the per centage of this gas in common atmospheric air was 20.833. The approximation of this determination to that attained at the present time, by the aid of the delicate balances which our scientific mechanics have furnished us, is most wonderful, and can be only understood when we recollect that it was the result of many hundred analyses of the air made during sixty successive days in the year 1781, by this indefatigable experimenter.

In Pneumatic Chemistry, or the chemistry of the gases, although he is considered the fourth in order of time among the English chemists—the other three being Hales, Black, and Priestly—yet he is entitled, on the score of discovery, to a rank along with the first. Dr. Wilson very truly says, "We have done little more in later times than extend, improve, and,

as we complacently say, *perfect* Cavendish's processes for the analysis of gases, and that we differ from him more in our mode of interpreting certain of the phenomena he witnessed than we do in our methods of investigating elastic fluids." His thorough knowledge of a proper *modus operandi* with the gases made him adopt the securest methods of experimenting, so as to allow of the least possible chance of a failure. Accordingly we find that, despite of the imperfection of apparatus (which was exceedingly imperfect and complicated), despite of the general ignorance of both physical and chemical properties of the gases, despite of the thousand and one difficulties that at all times beset the discoverer's path, the experiments of Cavendish were accomplished with an accuracy that our better knowledge of the subject, and command of more perfect apparatus, scarcely make us capable of excelling. In the school of these experiments, his attention was directed to the rationale for the formation of globules of water whenever the electric spark was passed through a mixture of hydrogen gas and atmospheric air, the result of which was the announcement of the greatest discovery of modern times, that of the exact composition of water—and one on which, in our opinion, the present character of chemical science rests as its true basis—without which the whole of analytical chemistry would be at best but a series of shrewd guessings at the composition of material substances, and synthetic chemistry would be confined to the *accidental* formation of substances, instead of that series of sure results with which we find it now abounding.

I call the announcement of the discovery of the composition of water the initial point in the history of rational chemistry, whether we view it in the departments of analysis or synthesis, in medical chemistry, or chemistry applied to the arts. Prof. Playfair has not gone too far when he stated in his lecture before the Society of Arts, Manufactures, and Commerce, that "the discovery of the composition of water has given to Industry a vitality and an intelligence, the effects of which it would be difficult to exaggerate."

Let us briefly examine the history of this discovery, and then see in what way it has been of so much importance to mankind. In doing this it is not desirable that we should involve

ourselves in the polemic arguments that have been brought forward by the friends of two other great men, who are said to have made the discovery prior to its announcement by Cavendish. Much ill-feeling has been excited by the friends of Watt and Lavoisier on this subject, and no less a person than M. Arago has taken the position that Watt really was the discoverer, and that Cavendish had filched all his knowledge of the composition of water from a letter which Priestly had received from Watt. Without going into an examination of this serious charge, which would involve a tedious enumeration of many circumstances to us of no interest, and which would only lead us to the conclusion arrived at by all impartial English observers, that Cavendish was the prior discoverer, we need only say that the charge of plagiarism is entirely dissonant from the general character of this great man, who seemed under all circumstances equally careless of praise or blame from the world.

Priestly and Warltire found, whenever hydrogen gas and atmospheric air were exploded by the electric spark, that there was a deposition of moisture on the inside of the vessels containing the gaseous mixture. Prior to this, however, Macquer, in 1766, observed that whenever a glass vessel was held over a burning jet of inflammable gas, that moisture was formed inside of the vessel. Warltire explained this by the supposition that the gases contained some water diffused through them, and that this, being condensed, appeared in drops on the sides of the containing vessel. Cavendish found that there was no diminution or increase of weight in the vessel after the explosion, but that a volume of hydrogen twice as large as the oxygen in the air had disappeared, that it had left its gaseous condition, and was converted into water. He performed the experiment on a still larger scale, so that this fluid might be examined, and arrived at the conclusion "that this dew is plain water." The after-course of his experiments was directed to the determination of the quantities of hydrogen and oxygen necessary to form water. He discovered that if one volume of oxygen and two of hydrogen were exploded in any way, the result was the conversion of the whole of the mixed gases into water.

Now, how does this discovery, so disconnected at first sight



from the other facts of chemistry, affect the whole progress of the science? How does the simple fact of the knowledge of the true composition of water bear so important a part in the progress of chemistry as to be considered by any one as the initial point in the history of this branch of study as a science? Might we not have a knowledge of all the other elements, and yet remain under the belief that Aristotle and thousands of his followers held, that water was an elementary substance? Could we not have unfolded the arcana of nature without first having cleared up this point, and considered the bland agent which nature uses in effecting the wonderful works of change as an elementary substance?

To all of these interrogatories, the more we think over the subject, the more impressive and emphatic must be our negative. Nothing could have been done which would not have been involved in all the mystery and obscurity that marked every result of the chemist's labors prior to the year 1781. And this is perfectly apparent, when we reflect over the paltry theory of Stahl, as to combustion, which was at that time leading all the world into a maze of confusion with its queer reasons for the combustion of a body, because it had a *something* called phlogiston in it, which regulated the duration of the combustion by the amount present, and when all of this substance escaped, *then* the body ceased to burn. It was necessary to have some plausible, and not only plausible, but some correct theory of combustion, as well as some account of the composition of water. These were both furnished by Cavendish's experiments.

In order to understand *quantitatively* the composition of bodies, it is necessary to get the combining number of some one elementary substance,—to have that well ascertained, and then we are ready, by the known laws of chemistry, to ascertain the combining numbers of all bodies, with which this particular substance forms combinations. In other words, the *equivalents* or *atomic weights* of all the elements could never be obtained had we not that of one single element to commence with. But it would be impossible to obtain the combining number of an element, without experimenting with it when in a state of combination, and hence it is necessary in order to

obtain these numbers, in which all certainty in quantitative chemistry is founded, that we should have a certain knowledge of the weights with which two elements combine in the formation of some known compound. This could be done in the case of water, after the compound nature was once fully understood. A Dalton could weigh the constituent elements and find that the oxygen always weighed eight times as much as the hydrogen, although the latter was twice as much in bulk. After experiments proved that these numbers, 8 and 1, indicated the only proportions in which these two elements would unite with any other elementary substance, and that each one of the others had also a number peculiar to itself, indicative of its combining proportion. And so, *on this discovery*, we may say, was reared that essential guide to all our chemical labors, the atomic theory.

It was a grand discovery, to find that all the substances in nature were allowed only to combine with each other in fixed and definite proportions, and that thus, instead of an infinitude of compound bodies, produced by an heterogeneous union of the elements, the number was to a certain extent fixed and immutable. The proportions with which they combine together is capable of being expressed in numbers. The chemical constitution of all matter becomes, when viewed in this light, beautifully illustrative of the poetry of science. No longer need we leave our own planet to behold this poetry of science, and, with the astronomer, roam through the wide circuit of the universe, as it, with silent grandeur, acts its epic in the measured numbers which his science reveals with so much accuracy. For though our knowledge of the mighty orbits of planets, and the perturbations which these occasion on each other's movements, impress us strongly with the harmony which pervades all creation and enable us to understand what the ancient philosopher spoke of as the Music of the Spheres; yet is not this harmony confined only to the movements of these great bodies, but permeates every particle of their structure, and beautifully governs the composition of all matter.

The slightest change in the composition of a body is sufficient to alter its nature as an innocuous substance, so that it shall become a deadly poison. Add but one atom of hydrogen

to the atom of water, cause a chemical combination to take place between the two, and instead of a supporter of life, and a substance necessary to the life-giving circulation of plants and animals, we find a poisonous substance of so caustic a nature, that when brought into contact with the tongue it produces at once a powerful burning sensation. Fortunately for all living beings this combination is not readily effected, nor is the compound a very persistent one. Otherwise we should be in danger of being poisoned by the very substance which is now the blandest in nature. How well does this fit us to understand the beautiful remarks of Farraday, as to the effects of a knowledge of these facts on the contemplative philosopher? "When I consider," says this distinguished savan, "the multitude of associated forces which are diffused through nature—when I think of that calm and tranquil balancing of their energies which enables elements, most powerful in themselves, most destructive to the world's creatures and economy, to dwell associated together and be made subservient to the wants of creation—I rise from the contemplation more than ever impressed with the wisdom, the beneficence, and grandeur, beyond our language to express, of the Great Disposer of all."\*

What an argument against the existence of blind chance is this exact proportion in which elements will alone unite with each other! How consummate a wisdom is thus shown in the formation of the smallest atom of water, which, wherever found, exhibits the same composition. The comtemplative chemist finds himself overcome when he sees the wonderful wisdom, that not only knows the fall of the sparrows to the ground, but has assigned eternal laws to the structure of every atom of that ground itself.

I have assumed here that the full knowledge of the composition of water led to the discovery and announcement of the atomic theory. It was not the special substance under examination by Dalton when the theory suggested itself to his mind; for that was the composition of the compounds of nitrogen and oxygen. But these could not have been understood unless Cavendish had prepared the way for it by first explain-

\* Farraday's Lectures, p. 191.



ing the composition of water. It is proper that this explanation should be made lest a charge of innaccuracy be brought with reference to our statements. The atomic theory was the indirect result of this great discovery of Cavendish.

But we have said the discovery of the composition of water was an initial point in the history of rational chemistry. What has been done by this science in the last seventy years? The answer to this question will show the importance of the discovery. In framing such an answer, the difficulty is to know where to commence, since chemistry has intertwined itself so much with the progress of every science, that its benefits are hardly to be appreciated by us unless we closely examine the history of the past, and after having obtained a full knowledge of the comparative ignorance of those days, then look around us and see the blessings which science has showered on us in the present.

Every art has been supplied with a knowledge of all the substances that enter into the composition of the materials it employs, or the tools necessary for their proper working. The perfection of processes, which were formerly dependent entirely on the chance combination of proper quantities of the materials employed, is now so great that empiricism has ceased its rule in the mechanic arts, and the chemist's discoveries constitute the bases on which these are constructed with their huge proportions and wonderful adaptation to the wants of man.

The *materia medica* is being gradually explained, and its potent extracts, obtained through the aid of pharmaceutic chemistry, are now employed by the scientific physician to the alleviation or cure of disease. He finds himself no longer confined to a mere empirical exhibition of enormous quantities of drugs, but more elegantly and efficaciously uses their proximate principles, while he rejects their inert constituents. But more than this yet, many of the recondite processes of the living body have been determined to be purely chemical, although regulated by the vital force, and hence he learns to produce such modifications in them as are required when disease has forced them to assume an abnormal form. Much thus of philosophic, rational medicine owes its origin to these

improvements of chemistry. The physician of the present day who neglects its teachings, gropes along his path with a blindness that is as pitiable as it is unjustifiable. He blindfolds his eyes to keep out the glorious sun-light of science, which is shedding a dazzling radiance over the pathway of his brethren ; he wanders along alleys and bye-ways, when the straight and broad highway could bring him at once to a terminus of all his labors ; he prefers darkness to light, and by some peculiar mental obliquity is prevented from adopting the direct path, but works along in the circuitous meanderings of that curse—*Routine* ! He has joined himself to the ignorance of the past, and rejected the knowledge of the present, and an inward turning of all thoughts on the past, has made him “ the man behind the age ”—a species of skeleton in the social circle of his profession, from whose bones and worm-eaten ligaments his brethren can demonstrate to their students what was the structure of medicine before the spirit of science entered it, and made dry bones to move, clothed them with muscle and cellular tissues and skin, caused artery, vein, and nerve to ramify around them, and infused the breath of active, thoughtful life.

Analytical Chemistry has revealed to us the quantities of the various elements which enter into the formation of the inorganic kingdom, and also of many portions of the organic kingdom, and has enabled the chemist, by synthesis, to form inorganic compounds, far exceeding in number and variety those found in nature, and of varied uses to mankind. Indeed, it has enabled him to use the various agencies of nature in so many novel ways, that new branches of art have sprung up all over the world, which have given thousands of artisans constant and profitable employment. Chemistry has become a science of most certain vitality, and gifted with the power of imparting its vitality to every branch of human industry with which it has anything at all to do. The artisan must feel its importance, and he desires his children, male and female, to have a knowledge of its principles, so that they can avail themselves of the discoveries of the day as they appear, and have an intelligent appreciation of their bearing on what has been done in the past, or may be expected to be done in the

future. Hence it is one of the branches of study which occupies a prominent place in any well-digested system of education, bearing with it the interest which always is attached to the study of anything that directly concerns man as man, and which is capable of illustration in an experimental way. Popular lectures on the subject are devised to meet the want with those who had not the means of studying the subject in their school-days, and the crowds of ladies and gentlemen attending these lectures attest the general interest of the community in a subject so manifestly important as chemistry.

Surely all this, if it has had its origin in the impetus given to the study of chemistry by Cavendish's discovery, must surround the latter with so much importance that no excuse need be given for the introduction of the name and character of Henry Cavendish to the present audience.

But we have not done with Cavendish as a chemist. We must not forget that his right to the discovery of hydrogen gas, as a *distinct* element, is undisputed, even by his enemies, although they have endeavored to rob him of the priority of the discovery of the composition of water. This gas was known prior to his day, and Thomson considers its combustibility as known at the beginning of the eighteenth century.

Cavendish, in the commencement of his observations, labored under the disadvantages which clung to a student of the Phlogiston theory. He found that an inflammable gas was freely discharged whenever iron, zinc, or tin were brought into contact with dilute sulphuric or muriatic acids, and quaintly says: "Their phlogiston flies off without having its nature changed by the acid, and forms the inflammable air."\* He imagined thus, at first, that the heating principle of bodies was this phlogiston, which was supposed to fly off during the phenomena of heat and light, and that when metals were plunged in either of these dilute acids, it escaped in the form of an æriform body, which he called inflammable air. Afterwards, however, he advanced the idea that inflammable air was a combination of the mysterious phlogiston and water. Its different properties were carefully examined—the circumstances under which it would burn, and how much atmospheric air must be present, in order

\* Wilson's Life of Cavendish, p. 197.



to allow of perfect and entire combustion of the gas were carefully noted. Not being satisfied with this, he advanced to the discovery already noticed, and finding it a constant constituent of water, arrived at the conclusion that the gas given off, whenever the metals mentioned were brought into contact with dilute acids, was furnished from the water with which these acids were diluted. His views as to the real nature of the gas, divested of the foolish nomenclature of the Phlogiston School, show that he had a clear idea of its nature and properties.

During his examination of the gas, his attention was directed to its weight, and he made, according to his biographer, "the first *successful* attempt to compare the density of a gas with that of common air." The attempt had been made previously by Hawksbee and Greenwood, as well as Hales. Their attempts failed for various reasons. It was left, however, for the mind of Cavendish, which was essentially mathematical, to devise such processes and apparatus as would enable him to experiment without any fear of failure. Quantitative examinations were those alone which satisfied his mind, and to the test of weight and measure he endeavored to bring every subject which he examined, not being content until some satisfactory answer was obtained from this test. Hence he was the first who found out that the different gases have, for equal bulks, dissimilar weights. His estimate of the specific gravity of hydrogen was found entirely too large, as he made it about one-eleventh of atmospheric air, whereas the latter is about 14.4 times heavier than it. Such a near approximation, taken into consideration with the necessary imperfection of apparatus at that day, and the probable imperfect removal of atmospheric air from the vessel into which the hydrogen was admitted, must entitle our chemist to the greatest praise for his accuracy, instead of blame for a want of accuracy.

The next subject we find him examining with his usual care and patience was carbonic acid, or fixed air as it was then called. It would be difficult to say who was first acquainted with this acid gas. Paracelsus seems to have known some of its properties, though its name of fixed air was given by Dr. Black, who examined it prior to the date of Cavendish's ex-

periments. Black seems, however, never to have published any account of its properties in general. In 1766, Cavendish took up the subject, and prepared the gas for examination by the action of chlorhydric acid on marble, a method still adopted by the venders of carbonic acid water as the most economical and convenient. His researches resulted in the acquisition of a full knowledge of all its properties, even getting the specific gravity very nearly correct.

We must recollect that experiments could not be carried on then as now, with the aid of numerous laboratory appliances, such as glassware of an infinite variety of forms, the multifarious uses of illuminating gas for heating purposes, and the convenient purposes to which caoutchouc is applicable. The modern chemist is supplied with a vast deal to assist him in his researches which the chemist of even fifty years since was not able to command. Consequently, even approximate accuracy in the latter merits much higher praise than perfect accuracy in the former. Continued demand for scientific apparatus has stimulated the mechanic to contrive various means for meeting the chemist's wants, and this he has succeeded in doing so well, that every day affords some fresh evidence of his skill, and the useful assistance he can render to the chemist.

While Cavendish was performing his experiments with reference to the composition of water, by passing an electric spark through a mixture of hydrogen and atmospheric air, he came across a singular result, which had been altogether unexpected. The water produced by the explosion was found possessed of acid properties. This was proven by its converting the blue color of litmus into a red, and by its combining with lime and forming a salt. It was nitric acid. Whence could it have been derived? He followed this query with great care to its ultimate bearings, and soon saw that the electric spark produced an union of the two gases, nitrogen and oxygen, in the proper proportions to form this acid. The fact has been proven in a number of ways since Cavendish's day. Farraday\* "has shown that if a piece of paper dipped in a solution of caustic potash be stretched a little below and between two brass balls, from one of which electric sparks are passing to the other, the

\* Life of Cavendish, p. 261.

alkali will be rapidly converted into nitrate of potassa, and the paper become touch-paper."

This discovery was probably one of the greatest contributions he made to the cause of science, and it proceeded as a necessary consequence from the experiments with reference to the constitution of water. We have here a clear explanation of the appearance of nitric acid, to a greater or less extent, in all rain water. The passage of the electric current in every thunder-storm repeats, on a large scale, this experiment of Cavendish, and produces a small quantity of nitric acid. This however, only takes place directly along the track of the lightning; and hence but a small quantity of this poisonous acid is formed in the atmosphere, is absorbed by the rains and descends to the soil. But the electric flash does not only, as Cavendish thought, cause the union of the nitrogen and oxygen so as to form nitric acid, but if hydrogen be present also, it causes an union of the nitrogen with it also, and the consequence is the formation of ammonia, which neutralizes a large quantity of the nitric acid, and descends in the rains to invigorate the exhausted soil as nitrate of ammonia. It is not always easy to account for the appearance of this substance in the soil, unless we had been prepared by these views of Cavendish, to account for its formation in the atmosphere, and after transference by the rains to the soil. Nitric acid does not form a constituent of any rock which is widely distributed over the surface of the globe, and yet the nitrates are found always in fertile soils, and in some tropical climes, where there are frequent storms, the quantity becomes so notable that thick incrustations are found on the surface. This acid in the nitrate seems to have considerable effect on the growth of plants, and to be indeed a most indispensable constituent of good soil. Its presence in the soil, as conveyed to it from the atmosphere, is beautifully explained by the aid of this discovery of Cavendish. Prof. Johnston\* remarks, on the subject of the formation of nitric acid: "After a thunder-storm plants appear wonderfully refreshed; in thundery weather they grow most luxuriantly, and other things being equal, those seasons in which there is much thunder are observed to be most fruitful.

\* Johnston's Lectures on Agricultural Chemistry, p. 160.



Some have ascribed these results to the *immediate* agency of electricity on the growth of plants. Is it not equally possible that they may be connected with this necessary production of nitric acid." The Professor then goes on to state that this acid is difficult to detect in minute quantities; yet "how much must be formed in a thunder-storm, even in our climate (Great Britain), to make the presence of this acid *always* appreciable in the rain that falls—how vast a quantity in those warmer climates where such storms are so frequent and so appalling." Thus the agricultural profession has been supplied with a capital explanation of a most important subject, and the import of Cavendish's discovery is much more than he could have dreamed of. The importance of this discovery is still greater when we view it in its direct bearing on the question of the combustibility or not of nitrogen.

Cavendish's formation of nitric acid out of nitrogen, in the way just mentioned, proved conclusively that this gas could be oxidated under certain circumstances, or that it could be subject to combustion, using the latter term in its widest chemical signification. This has been seized hold of by Liebig and Johnston, and made also to subserve the purposes of agricultural chemistry, in the way of accounting for the immense quantity of nitric acid contained in some soils, far beyond that which could possibly be formed from the action of electricity on the atmosphere. Whenever organic matter containing nitrogen undergoes the processes of decay or putrefaction, ammonia is formed from the hydrogen of the water present, and this nitrogen. But this ammonia is rarely found present in very large quantities, although large quantities of nitric acid are readily recognized, and mostly in connection with alkaline bases, making nitrates. In fact, the presence of these alkaline bases determine the metamorphosis of the ammonia into nitric acid, through the combustion or oxidation of its nitrogen. The alkaline bases induce, so to speak, "this oxidation, by the tendency of these substances to combine with the acid which is formed by this union of the elements of which nitric acid consists." \*

This explanation of Liebig, based on Cavendish's discovery,

\* Johnston's Agricultural Chemistry, p. 163.

beautifully illustrates the immense importance any discovery in science may be to *present* and *after* investigations, and also how little able a discoverer is to realize the importance of the fact he has attained after long and toilsome research. Truth is indeed of such a nature that its value stops not at one point, but by inosculation many and various, extends its aid to all branches of knowledge, and binds them together by a common bond, so that what is useful to one branch will be seen alike important and useful to all, and *catholic* in all its peculiarities.

When we sum up the peculiarities of Cavendish as a chemist, we find them to be as follows : A mind perfectly free from all foregone conclusions, and hence specially suited to carry out new lines of investigation, and to interpret properly the meaning and bearing of the results therein attained. This is by no means one of the least important peculiarities of mind required by the experimenter. How many ridiculous estimates have been made of the results of experiments, merely because the glasses through which the experimenter viewed them, had been previously so colored that their true form and nature could not be clearly recognized? Thus monstrous theories have been warmly maintained because their authors have determined that such and such results should be produced by their experiments. The real nature of the results has been overlooked, and men have been led astray by their false interpretation, until some mind, unprejudiced by theories of its own, has examined them carefully, and has sifted them from all irrelevant matters, and arrived at the simple truth. The history of chemistry, past and present, is teeming with illustrations of this kind, and many really important discoveries have been overlooked while some apparent confirmation of an unsubstantial theory has been seized as pure gold by the blinded experimenter. Indeed, it is one of the most difficult of all things, to elaborate a course of experiments, with a mind perfectly freed from all disposition to give a certain complexion to the result, and to truly interpret only so much as is really presented by it. Too often the result is but used as a mirror, in which the chemist only sees his own darling idea reflected, without paying any attention to the real nature of that mirror, or to the obli-

quity of his vision, which is but viewing a projection forth of his own ideas in all their unsubstantiality, rather than the truth involved in the material form before it. Such was not the habit of Cavendish. Mistakes were frequently made as to the results of experiments, never on account of any peculiar theory to which he was determined, to bind them as illustrations, but on account of the slight knowledge which the world possessed of chemistry, and therefore its inability to recognize, at first sight, the full meaning of its facts. But repetition of his experiments enabled him to see errors, and to place himself right as to his conclusions. On this account he never published a paper on any subject until he examined his own views with the sternest critic's eye, and forced them to undergo the severest tests. There was no disposition to enter a *caveat* against any one's poaching on his grounds—no use of the meetings of scientific societies or the pages of scientific journals for the publication of ill-digested opinions on novel results of experiments. But all his published manuscripts show that they have been carefully digested—his opinions freed from all irrelevant matter, and tried and approved by, or rather based on experiment. The author of "Pursuit of Knowledge under Difficulties," says that "he never advanced anything in any of his papers which he had afterwards to retract."

It is evident also that, in addition to a mind free from any bias in the examination of his experiments, he was a careful manipulator. His apparatus was of the simplest character. He took no delight in complications of apparatus, which only impress the eye with their complexity and weary the operator. His mechanical skill as a deviser of new forms of apparatus was exceedingly small, but he had the still happier facility of adapting the old forms to his own purposes and making them available. Hence all the apparatus which has descended to our time from the laboratory of Cavendish is marked with great simplicity and even want of finish.

Another peculiarity of Cavendish as a chemist, and which has already been incidentally alluded to, was his fondness for quantitative determinations of all substances which he examined, and the accuracy of those determinations. This must have been the result of a mathematical turn of mind, which he



derived from his father, Lord Charles Cavendish, who was an excellent mathematician, "who had devoted himself to meteorology, and had paid special attention to the improvement of the thermometer and barometer, so that our philosopher was easily trained to the points essential to the accurate construction and employment of these instruments." This mathematical turn of mind caused him to combine the study of physics with that of chemistry, and the subject of electricity and the aurora borealis were well treated of by him. But its greatest influence was in the determination of accurate quantities in his examinations. The quantitative analysis of the air compares well with those since made with the best laboratory appliances. The specific gravity of carbonic acid gas, as determined by him, has already been shown to be approximately correct, and this is true of every quantitative determination.

If mathematical accuracy, great care and simplicity, and an unprejudiced mind, are essentials in the composition of the chemist, surely we have them here, combined in a most wonderful manner in the case of Cavendish. We are now led to see how these, with his remarkably original turn of mind and powerful intellect, enabled him to tower above his scientific compeers—to write his name high up among the benefactors of mankind, and to have a reputation as a scientific man which it must ever be the jealous care of his brethren to maintain with its original brilliance.

A few words on his character as a man and the cause of his peculiarities, and our task is done.

One of the most remarkable traits in the character of Cavendish was his extreme diffidence and indifference to society of all kinds. He was scarcely ever found in society, and never willingly entered into conversation with the opposite sex. This was carried to so great an extent that he never communicated orders to his female servants directly, but by means of a note directed to his housekeeper. An anecdote quoted by his biographer, Dr. Wilson, from Tomlinson, illustrates this perfect misogyny in the most amusing way. "One evening," says Tomlinson, "we observed a pretty girl looking out from an upper window on the opposite side of the street, watching the philosophers (the members of the Royal Society Club) at din-

ner. She attracted notice, and one by one we got up and mustered round the window to admire the fair one. Cavendish, who thought we were looking at the moon, bustled up to us in his odd way, and when he saw the real object of our study, turned away with intense disgust, and grunted out 'Pshaw!'" Dr. Wilson suggests as the origin of all this want of sympathy, that he lost his mother in early life, and that he was brought up away from the genial and humanizing influences of home. The explanation is exceedingly probable, for we cannot conceive how any one who has learned to appreciate the kind care of a mother, to prize those genial effects her sweetness of character and gentle disposition have produced in his own, to adore the purity of thought and feeling that so sweetly marks her life, without feeling the highest respect for the sex, whose gentleness is so much more powerful than our strength, that the stout man is often caused to bend the knee before it, and feel his own real moral weakness from the contrast. The man that has loved a mother can never have a low appreciation of the sex, if it were only for her sake.

But with all Cavendish's retiring habits he was exceedingly liberal, not knowing exactly how much he *should* give when solicited for a benevolent object, but always giving as much as any name on the subscription list. An anecdote of his liberality is given by Cuvier. A young man had broken a very valuable piece of apparatus, and the keeper of his apparatus came to tell him of it—the only answer he received was, "it is necessary for young men to break instruments, in order that they may learn how to use them—have another one made."

Routine marked his daily habits, which were the same for the greater portion of his life. The same style of clothing, the same place for his household affairs, even the same bill of fare for his dinner—truly has he been styled "a piece of intellectual clock-work"—that was not intended to produce any effect on mankind in any other department than that of pure knowledge. He has gone to his grave—one of the most distinguished of the benefactors of science—unwept, although honored.

It was thought that an examination of this great man's character, and his most important discovery would be useful,

at the opening of our course on chemistry, since his name must be occasionally mentioned, and the sources from which information with reference to his life is to be gained, are but few. Large draughts of material have been made from the very fair and impartial account of his life by Dr. George Wilson, which is accessible to but few in this country.

It is pleasant to treasure up the little incidents connected with the history of great discoveries, and the lives of their authors. If the latter, in a social respect, does not inspire us with as much love and regard, as would a close examination of the life of one more peculiarly belonging to this <sup>century</sup> ~~country~~, that of Sir Humphrey Davy ; yet, we can profit by it, if we only learn to avoid the blemishes in our own character, which were so prominent in that of Cavendish.

Gentlemen, our science is connected with so many departments of research, that it demands the attention of every man, but most especially that of those who propose to themselves to adopt the profession of medicine as their calling, or rather those who feel themselves *specially called* to its study, for none others should enter the ranks of medicine. If the example of Cavendish stimulate you to the cultivation of chemistry with methodical accuracy and care, your results, if not so striking and imposing as his, yet I am bold to say, will be important in fitting you for your noble calling. The moral heroism of our profession, as exhibited from time immemorial, during the visitation of destructive scourges, and most especially within the season just past, is sufficiently great to demand the admiration of a gazing world. May you all be ready to exhibit the same unflinching attention to duty, having previously prepared yourself by honest and laborious study to accomplish such duty ! May the results of all your *studies and labors*, in the various branches of the professional preparation, fit you to become, not only great men, but what is much better, good men, useful physicians, each a hero in his sphere.



*Chemistry*

# NOTICE

SUR

UN PROCÉDÉ PERFECTIONNÉ DE FABRICATION

DE LA

*54343*

# SOUDE ARTIFICIELLE

ET DE

## L'ACIDE SULFURIQUE,

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STRASBOURG,

IMPRIMERIE DE G. SILBERMANN, PLACE SAINT-THOMAS, 3.

1855.



# NOTICE

SUR

UN PROCÉDÉ PERFECTIONNÉ DE FABRICATION

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# LA SOUDE ARTIFICIELLE

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# L'ACIDE SULFURIQUE.



La fabrication de la soude artificielle et de l'acide sulfurique constituant une des industries les plus importantes, il est naturel qu'elle ait été, dans ces derniers temps surtout, le sujet de nombreux travaux et de perfectionnements intéressants; cependant il est facile de constater que l'ancien procédé de Leblanc est encore toujours, à quelques légères modifications près, celui qui est suivi par les manufactures les plus considérables.

Ce fait provient de diverses causes, dont les principales sont : le haut degré de perfection auquel est parvenue la fabrication de l'acide sulfurique; la condensation très-parfaite de l'acide hydrochlorique qu'on a obtenue au moyen des appareils et tours à condensation, et les nombreuses applications de cet acide; le bas prix des matières (chaux et combustible) et la simplicité des appareils exigés pour la transformation du sulfate de soude en carbonate sodique; enfin, la circonstance que la fabrication de l'acide sulfurique, combinée à celle de la soude artificielle et de la chlorure de chaux, forme un tout bien complet, bien symétrique, dans lequel presque tous les produits s'utilisent, soit par la vente directe, soit par la réaction des uns sur les autres.



Cependant le procédé Leblanc offre plusieurs désavantages, universellement reconnus ; le principal est qu'il entraîne la perte à peu près complète de tout le soufre contenu dans le sulfate de soude ; ensuite, il donne naissance, en énorme quantité, à un produit n'offrant que fort peu d'applications, et qui, par ses qualités infectes et nuisibles, est souvent la source de grands embarras et dont on a quelquefois de la peine à se débarrasser ; enfin, le traitement des matières dans les fours à calcination pour la préparation de la soude brute est assez difficile, et la bonne réussite dépend beaucoup de l'habileté et de l'attention des ouvriers.

Les plus importantes améliorations qui aient été proposées pour la fabrication de la soude artificielle au moyen du sel marin, l'ont été en vue de remédier au défaut principal du système Leblanc, c'est-à-dire à la perte totale du soufre. Tantôt on a essayé des réactions diverses dans le but de se passer complètement de la transformation préalable du sel marin en sulfate de soude au moyen de l'acide sulfurique ; d'autres fois on a substitué à cet acide des sulfates de peu de valeur ; enfin, on a cherché à dégager le soufre de l'oxisulfure de calcium à l'état d'hydrogène sulfuré, qui, brûlé, donnait ensuite naissance à de l'acide sulfureux ; d'autres perfectionnements ont eu pour but une condensation plus parfaite de l'acide hydrochlorique, l'emploi des pyrites naturelles à la place du soufre, une saturation plus complète de la soude par l'acide carbonique, l'élimination ou la destruction du sulfure de sodium dans les lessives sodiques, enfin, une richesse plus grande de carbonate de soude pur dans les sels de soude du commerce.

Si ces inventions et perfectionnements n'ont pas été plus généralement adoptés par la pratique, cela provient de ce que souvent ils dérangent cette économie et cet ensemble symétrique des opérations dont nous avons parlé plus haut, de ce qu'ils exigeaient l'emploi de substances ou d'appareils plus coûteux que ceux usités dans le procédé ordinaire de fabrication ; ou enfin, de ce qu'ils ne s'appliquaient seulement qu'à certaines circonstances ou certaines localités particulières. Le nouveau procédé que nous allons décrire nous paraît exempt des différents inconvénients que nous venons de signaler.

En effet, il présente les avantages suivants :

1<sup>o</sup> Il permet d'opérer avec les appareils et fours actuellement employés dans le procédé ordinaire de fabrication de la soude artificielle et de l'acide sulfurique.

2<sup>o</sup> Il dispense de l'emploi de la chaux et de la craie, et par là même évite complètement la production de l'oxisulfure de calcium, source de pertes et d'inconvénients nombreux pour beaucoup de fabriques.

3<sup>o</sup> Il permet de recouvrer tout le soufre renfermé dans le sulfate de soude et de le reconvertir avec une grande facilité en acide sulfurique.

4<sup>o</sup> Il rend toute perte d'alcali impossible, puisqu'il n'y a plus de résidu qu'on soit obligé de jeter.

5<sup>o</sup> Enfin, il rend la préparation de la soude plus indépendante de l'habileté des ouvriers et permet d'opérer, dans le même temps et avec les mêmes appareils, sur des quantités de matière plus considérables.

Le principe de l'invention consiste dans la fabrication, au moyen du sulfate de soude, d'une soude brute métallifère, au lieu de la soude brute calcaire ordinaire.

Cette nouvelle soude brute métallifère, traitée d'une certaine manière, produit d'un côté une solution aqueuse de carbonate de soude, et de l'autre côté un résidu insoluble de sulfures métalliques; ces sulfures métalliques grillés convenablement fournissent, de leur côté, un résidu d'oxides et du gaz sulfureux, qui est converti en acide sulfurique dans les chambres de plomb ordinaires. Cet acide sulfurique sert à convertir du sel marin en gaz hydrochlorique et en sulfate de soude, et au moyen du sulfate de soude et des oxides métalliques, on reproduit une nouvelle quantité de soude brute métallifère.

Il en résulte que dans une fabrique, opérant d'après ce procédé, en supposant qu'il n'y ait point de pertes, des quantités indéfinies de sel marin peuvent être converties en carbonate de soude et en acide hydrochlorique, n'exigeant pour cela que du combustible et la quantité de nitrate de soude nécessaire pour transformer l'acide sulfureux en acide sulfurique.

Les détails suivants suffiront pour donner une idée claire de la marche des opérations, et je m'attacherai surtout à décrire

la fabrication de la *soude brute ferrugineuse*, le fer étant de tous les métaux celui qui présente le plus d'avantages, soit à cause de son bas prix, soit à cause des propriétés chimiques de ses oxydes et sulfures.

Les proportions indiquées sont celles qui sont employées dans une grande manufacture du Lancashire, en Angleterre (celle de MM. Blythe et Benson, à Church, près Manchester), qui produit plusieurs milliers de tonnes par an d'après ce nouveau procédé.

*Première opération. — Mélange des matières.*

On mélange assez intimement 125 kilog. de sulfate de soude sec avec 80 kilog. de peroxide de fer et 55 kilog. de charbon.

Il est évident qu'il n'y a rien d'absolu dans ces proportions et qu'elles peuvent varier suivant le plus ou moins de pureté du sulfate de soude, du peroxide de fer et du charbon.

Les observations suivantes suffiront pour guider le manufacturier, soit pour ce qui concerne les matières à mélanger, soit pour les proportions, soit pour le poids total du mélange.

Quant aux matières :

Le sulfate de soude peut, sans inconvénient, contenir des quantités plus ou moins grandes de sel marin, seulement, dans ce cas, il ne faudra ajouter le peroxide de fer et le charbon qu'en quantités proportionnelles au sulfate de soude pur et sec renfermé dans le sulfate de soude brut. On emploie ce dernier tel qu'il sort des fours à calcination (comme résidu de la réaction de l'acide sulfurique sur le sel marin), en ayant soin de concasser les morceaux trop volumineux.

Le peroxide de fer doit être pesé sec et en poudre assez fine ; il est important qu'il soit aussi pur que possible.

Pour la première opération, au lieu du peroxide de fer artificiel ou naturel (hématite, fer oligiste), on peut faire usage de carbonate de fer (fer spathique), d'oxyde de fer magnétique, de battiture de fer, ou même de grenaille de fonte ou de fer métallique ; mais, dans ce dernier cas, il faudra diminuer la quantité de charbon, puisque le fer métallique agit comme réducteur sur le sulfate de soude.

Comme on le verra plus loin, quel que soit le composé de fer



employé, même lorsqu'on s'est servi de fer métallique à la première opération, on n'a plus tard à opérer que sur le peroxide de fer.

Le mélange de sulfate de soude et de peroxide de fer qu'on obtient comme résidu dans le procédé qui consiste à décomposer le sel marin par le sulfate de fer, s'adapte admirablement à mon nouveau procédé de fabrication de la soude, puisque, si les proportions ont été choisies convenablement, on n'a qu'à y ajouter la quantité de charbon requise.

Quant au charbon, on peut faire usage, soit de charbon de bois, soit de coak, soit de menu de houille, de lignite ou d'anthracite, soit même de toute autre substance réductrice organique, seulement la quantité en devra augmenter, à mesure que le pouvoir réducteur diminue. En Angleterre, on se sert de menu de houille de qualité ordinaire.

Maintenant, quant aux proportions :

Il faut observer qu'il est indispensable d'employer une proportion de peroxide de fer telle que le fer qui s'y trouve puisse se combiner avec tout le soufre du sulfate de soude, pour représenter la combinaison  $SFe$  (200 soufre + 350 fer) : sur 9 de sulfate de soude pur et sec, il convient donc de ne pas employer moins de 5 de peroxide de fer pur et sec ; il est avantageux de mettre un petit excès d'oxide de fer.

Si le peroxide de fer contenait du calcaire, il faudrait préalablement l'en débarrasser en le traitant à froid ou à une douce chaleur par de l'acide hydrochlorique très-étendu et lavant ensuite parfaitement ; car la chaux, dans le cours des opérations, se transformerait successivement en sulfure de calcium, puis en sulfate de chaux, puis, de nouveau, en sulfure de calcium, etc., augmentant inutilement le volume des matières à manipuler, et consumant en pure perte du charbon et de la chaleur.

Le charbon ne doit pas être employé en excès, d'abord, parce qu'il favorise la présence du sulfure de sodium dans le sel de soude, et cela malgré l'emploi d'une quantité convenable d'oxide de fer, et ensuite, parce que l'excès de carbone restant avec le sulfure de fer, on obtiendrait plus tard, en grillant ce dernier, un acide sulfureux mélangé d'acide carbonique.

Il convient donc de diminuer la proportion du charbon, jusqu'à ce que l'on découvre dans les blocs de soude brute ferrugineuse la présence d'une très-minime quantité de sulfate de soude non décomposé.

Finalement, quant au dosage, c'est-à-dire quant au poids total du mélange à introduire dans le four à calcination, ce poids dépend principalement des dimensions du four; je ferai seulement observer qu'on peut opérer sur une charge une et demie et presque deux fois plus grande que celle usitée lorsqu'on prépare la soude brute calcaire ordinaire; cela provient de ce que la soude brute ferrugineuse se travaille beaucoup plus facilement, le mélange devenant bien plus rapidement pâteux et finalement presque liquide.

Les détails qui précèdent, permettent à tout fabricant de composer un mélange convenable et approprié aux fours et appareils déjà en usage.

#### *Deuxième opération. — Calcination.*

Le sulfate de soude, le peroxide de fer et le charbon, ayant été intimement mélangés, sont ensuite introduits dans le four à calcination, qui est exactement semblable au four servant à la préparation de la soude brute calcaire.

Pour utiliser complètement la chaleur, il convient que le four soit à deux et même à trois étages, l'étage inférieur étant celui le plus rapproché du foyer. Le four contient, dans ce dernier cas, simultanément trois charges qu'on fait successivement descendre, et qu'on remplace à fur et à mesure de l'extraction des charges calcinées et terminées au premier étage, voisin du foyer.

Le traitement du mélange dans le four est semblable à celui du mélange pour la soude brute calcaire, et les phénomènes observés sont presque identiques: la matière se ramollit, devient pâteuse, puis de plus en plus fluide, à mesure qu'elle est brassée et ramenée plus en avant vers le feu; des flammes jaunâtres se dégagent abondamment de tous les points de la surface en produisant une espèce d'ébullition; lorsque la réaction, qui a été très-vive, commence à se ralentir, lorsque les flammes

deviennent de moins en moins volumineuses et abondantes, lorsque la masse s'affaisse et devient tranquille, présentant l'aspect d'une pâte mince, homogène, semi-liquide, alors l'opération est achevée et l'on se hâte de sortir la matière du four et de la faire couler encore rouge dans une espèce de wagon en tôle, où on la laisse refroidir et se solidifier, après l'avoir couverte, pour la garantir un peu du contact de l'air.

Après le refroidissement, la soude brute ferrugineuse se présente sous forme de bloc parallépipède, d'un aspect noirâtre, plus ou moins poreux, très-dur et d'une densité assez considérable. Lorsque l'opération a été bien conduite, le bloc est très-dense, sa surface a un reflet cuivré, et lorsqu'on le brise, la cassure présente un aspect uniforme, cristallin, à reflet métallique verdâtre très-brillant.

### *Troisième opération. — Délitiation et carbonation.*

La soude brute ferrugineuse étant ainsi préparée, il s'agit de la traiter de manière à en obtenir, d'un côté, du carbonate de soude soluble, et de l'autre du sulfure de fer insoluble.

Si l'on voulait opérer sur elle comme sur la soude brute calcaire, c'est à-dire la concasser après refroidissement complet et épuiser les morceaux par un lavage méthodique à l'eau, soit froide, soit tiède, soit bouillante, on n'obtiendrait que de mauvais résultats. En effet, la masse se gonfle, devient très-volumineuse, difficile à laver, et ne fournit que des liqueurs peu chargées, colorées en brun noirâtre ou en vert foncé, ne s'éclaircissant que très-lentement au contact de l'air et renfermant beaucoup de soude caustique, accompagnée le plus souvent de sulfure de sodium.

Le lavage devient au contraire des plus faciles lorsqu'on fait subir à la soude brute ferrugineuse une altération très-remarquable, que nous appellerons *la délitiation* et qui constitue une des opérations les plus importantes de notre procédé.

Voici en quoi elle consiste :

Lorsqu'un bloc de soude brute ferrugineuse est abandonné sous un hangar à l'influence de l'air atmosphérique, on le voit bientôt se modifier profondément et avec d'autant plus de rapi-



dité que l'air est plus chargé d'humidité et d'acide carbonique.

La surface perd son éclat et son état compacte ; le bloc se fendille, s'effleurit et se recouvre d'une matière pulvérulente, volumineuse, noirâtre ou grise noirâtre, dont la quantité augmente avec une telle rapidité, qu'au bout de plusieurs heures le bloc entier se trouve recouvert et enseveli sous une petite montagne de la matière pulvérulente.

Cette transformation est produite par l'absorption simultanée d'oxygène, de vapeur d'eau et d'acide carbonique, en même temps qu'il y a dégagement de chaleur. Cette dernière est très-sensible à la main en l'introduisant à une petite profondeur dans la masse pulvérulente, jusque dans le voisinage de la partie non encore modifiée du bloc. Si l'on abandonne le tout à lui-même, bientôt la température s'élève au point qu'il y a ignition, sur-oxidation, la poudre prend un aspect rougeâtre, et en la lessivant on en extrait du sulfate de soude, renfermant seulement 10 à 15 p. 100 de carbonate de soude : le résidu insoluble se compose d'oxide de fer avec une certaine quantité de sulfure de fer.

Mais le résultat est tout différent si l'on prévient l'élévation de température, et l'on atteint ce but très-facilement en empêchant la poudre de s'accumuler autour de la portion non délitée du bloc, qui doit toujours rester à nu, et exposé à l'action de l'oxygène, de l'humidité et de l'acide carbonique. Dans ce cas, au bout d'un certain temps, tout le bloc s'est transformé en la matière pulvérulente délitée. Celle-ci, si elle est restée suffisamment longtemps à l'air pour se saturer complètement d'acide carbonique, fournit par la lixiviation une belle solution de carbonate de soude et un résidu formé principalement de sulfure de fer. Mais l'expérience en grand ayant démontré que la saturation par l'acide carbonique de l'atmosphère ne se faisait que lentement et qu'elle était accompagnée d'une légère suroxydation de la poudre délitée, il a été trouvé avantageux de saturer artificiellement cette dernière, en l'exposant à l'action d'un courant d'acide carbonique froid et humide. C'est cette opération que nous désignons sous le nom de carbonation.

La disposition suivante, extrêmement simple, satisfait par-

faitement aux meilleures conditions de délitation et de carbonation.

Au-dessus d'un sol parfaitement dallé et entouré de murs, on place, à deux mètres et demi de hauteur, un plancher à claire-voie, formé de grilles en fonte, dont les barreaux présentent un écartement de un à un centimètre et demi. Il est avantageux de creuser la terre à environ un mètre de profondeur, pour que la porte, menant dans cette espèce de caveau, soit à pareille distance au-dessus du sol et qu'on ait à descendre un plan incliné pour arriver sur les dalles. A deux mètres et demi au-dessus du plancher à grille, on établit une toiture, en ayant soin de pratiquer dans les murs qui la supportent des jours très-larges et très-nombreux, pour permettre à l'air d'y circuler et de s'y renouveler avec la plus grande facilité. L'air ne peut pénétrer dans le compartiment inférieur ou dans le caveau qu'en passant à travers les espaces que laissent entre eux les barreaux de la grille. Mais cela n'arrive guère, puisqu'on a soin d'y faire parvenir, par plusieurs ouvertures pratiquées dans les murs, un courant continu d'acide carbonique froid et saturé d'humidité. L'acide carbonique est produit en Angleterre, où fonctionne cet appareil, par la combustion complète de coak dans un foyer fermé, dans lequel l'air est chassé par un ventilateur; les produits de la combustion passent par des canaux en fonte, refroidis extérieurement et ayant les parois intérieures constamment humectées par un courant d'eau, et ce n'est donc qu'après avoir perdu sa haute température et s'être saturé d'humidité que l'acide carbonique arrive dans le caveau. Enfin, des dispositions sont prises, pour qu'en cas de besoin, lorsque l'atmosphère est très-sèche, on puisse entretenir humides, au moyen de filets d'eau, la partie intérieure de la toiture et des murs.

Voici maintenant comment on opère:

Les blocs de soude brute ferrugineuse, après complet refroidissement, sont amenés sur le plancher à claire-voie et placés debout sur une des petites faces; à mesure que le bloc se délite, la portion délitée pulvérulente tombe à travers la grille et s'accumule sur le sol dallé, où elle se sature immédiatement d'acide carbonique. L'absorption de ce dernier est tellement

rapide, qu'on n'a qu'à arrêter le ventilateur pendant une à deux minutes pour faire disparaître complètement tout indice de la présence de l'acide carbonique dans le caveau.

La portion non délitée du bloc restant ainsi constamment à nu et soumise à l'action de l'atmosphère, le bloc ne tarde pas à se fendiller et à se diviser spontanément en fragments plus ou moins gros. Chaque fois qu'un nouveau bloc est amené, l'ouvrier a soin de faire tomber à travers la grille la poudre délitée qui aurait pu s'accumuler au sommet de quelques blocs, et là où il ne reste plus que des fragments très-réduits de plusieurs blocs, il les réunit pour faire une place vide prête à recevoir un nouveau parallépipède de soude brute ferrugineuse récemment préparé.

Un bloc de 250 kilog. exige au maximum un mètre carré de place pour sa délitation, qui prend huit à dix jours pour être complète. Il s'en suit qu'un bâtiment long de vingt mètres et large de dix mètres suffirait pour 200 blocs, qui fourniraient plus de 50,000 kilog. de poudre en dix jours ou 5000 kilog. en un jour.

10 quintaux métriques de menu coak, valant en Angleterre de 7 à 8 fr., suffisent pour carbonater 90 à 100 quintaux de carbonate de soude sec et pur.

Dans des localités où le combustible est cher et la main-d'œuvre moins coûteuse, il peut y avoir avantage à laisser la carbonation s'opérer par le secours seul de l'atmosphère, en ayant soin d'humecter légèrement la poudre délitée et de la retourner fréquemment, ou bien on peut rassembler de temps en temps la poudre, l'humecter et la soumettre dans des canaux à l'action des produits gazeux un peu refroidis, qui proviennent des fours à calcination.

Quel que soit le procédé adopté, la matière délitée, prête à être lessivée, doit présenter les caractères suivants: elle doit être pulvérulente, fine, d'une couleur grise ou grise noirâtre, et ne doit point contenir de fragments plus gros et durs. Il est toujours avantageux de faire passer la poudre à travers un cylindre tamiseur, pour se débarrasser des matières pierreuses, qu'on lessive à part, ayant soin de rejeter le résidu insoluble. Les matières pierreuses ou terreuses proviennent ordinairement



du four à calciner ou du menu de houille. La poudre tamisée, agitée avec de l'eau froide ou tiède, doit former une liqueur qui s'éclaircit parfaitement au bout de cinq à dix minutes, laissant déposer un précipité lourd, d'un noir foncé, souvent à reflet cuivré, et fournissant une solution parfaitement claire, limpide, incolore ou tout au plus d'une teinte jaunâtre à peine appréciable.

*Quatrième opération. — Lixiviation.*

La lixiviation doit être faite méthodiquement, soit par filtration, soit par décantation, d'après les procédés rationnels parfaitement connus, au moyen d'eau tiède de trente à quarante degrés centigrades. Les solutions faibles sont employées à lessiver de nouvelles quantités de poudre délitée et carbonatée.

Lorsque la température extérieure n'est pas trop élevée, les solutions fortes fournissent généralement, sans concentration préalable, après vingt-quatre à quarante-huit heures, une abondante et belle cristallisation de carbonate de soude, en gros cristaux hydratés parfaitement transparents et incolores.

En jetant dans la liqueur refroidie un morceau de carbonate de soude calciné, on hâte souvent extraordinairement la cristallisation. Par l'évaporation à sec et une légère calcination, les eaux mères et les liqueurs un peu faibles donnent pour résidu un sel de soude tout à fait blanc, de 80, 85, 90 et même 95 p. 100, suivant qu'on a apporté plus ou moins de soin à la pureté des matériaux, au choix des proportions et à l'exécution des diverses opérations qui ont été décrites.

Le résidu des lavages, formé principalement de sulfure de fer, d'un aspect à la fois noirâtre et cuivré, ayant été à peu près complètement épuisé, est recueilli sur des filtres ou sur une surface poreuse, pour qu'il puisse s'égoutter le plus possible.

Dans cet état il ne s'altère que très-lentement; une fois égoutté, on peut le traiter de diverses manières; ou bien on le dessèche imparfaitement en couches pas trop épaisses sur des plaques chauffées, ou bien on se contente de le presser fortement, en lui donnant le plus convenablement la forme de briques. Ce sulfure de fer est tellement combustible, qu'il prend

feu même au-dessous de cent degrés et brûle comme de l'amadou, lorsque la dessiccation est poussée au point de devenir à peu près complète.

*Cinquième opération. — Calcination du sulfure de fer.*

La calcination du sulfure de fer se fait avec la plus grande facilité, soit sur des plaques de fonte chauffées au rouge sombre, soit mieux encore sur la sole d'une espèce de four à reverbère, ou de moufle de grande dimension, chauffés extérieurement. Il est très-aisé de disposer ce chauffage de telle manière que les produits de la combustion puissent être utilisés à la carbonation de la poudre délitée. Il est avantageux de diviser le four à combustion du sulfure de fer en deux compartiments, ou du moins d'introduire la charge en deux fois, pour que la calcination puisse s'achever d'un côté, lorsqu'on la fait seulement commencer de l'autre. On introduit le sulfure de fer encore légèrement humide et on ne le remue pas pendant la première heure. Il dégage d'abord de la vapeur d'eau, dont la présence favorise la formation de l'acide sulfurique, puis il s'enflamme et ne présente bientôt qu'une masse incandescente, dégageant des torrents d'acide sulfureux; lorsque la combustion devient moins vive, on remue de temps à autre la poudre avec un ringard en fer; en opérant ainsi, pas la moindre parcelle de fer n'est entraînée dans les chambres de plomb. Au bout de trois heures, la calcination est complète, et en sortant la matière du four, on trouve un oxide de fer rouge cramoisi, en poudre très-fine.

On comprend facilement comment la combustion de ce sulfure de fer peut remplacer la combustion du soufre ou des pyrites naturelles pour la préparation de l'acide sulfurique.

Quelques kilogrammes de ces derniers, brûlés additionnellement avec notre sulfure de fer, suppléeront facilement au déficit de soufre provenant soit de pertes accidentelles, soit de soufre qui aurait pu rester avec le sel de soude à l'état de sulfate ou de sulfure sodiques, ou qui aurait encore pu se dégager du peroxide de fer sous forme de gaz sulfureux après sa sortie du four à griller.

L'acide sulfurique préparé dans les chambres de plomb au

moyen de l'acide sulfureux dégagé dans le grillage du sulfure de fer, servant à décomposer une nouvelle portion de sel marin pour produire du sulfate de soude et l'acide hydrochlorique, il est aisé de comprendre comment, par l'intervention des oxides et sulfure de fer, le même soufre peut être utilisé un grand nombre de fois pour aider à la transformation du sel marin en carbonate de soude.

En réfléchissant à la circonstance que rien n'est plus jeté dans ce nouveau procédé de fabrication, on comprend que les impuretés du sel marin, du sulfate de soude, de la houille et les matières détachées des fourneaux et appareils doivent peu à peu s'accumuler dans le sulfure et le peroxide de fer; aussi au bout d'un certain temps est-il bon de renouveler celui-ci. Mais ce temps est beaucoup plus considérable qu'on ne serait disposé à le penser de prime-abord: on se l'explique, en observant que les impuretés les plus grossières sont éliminées par le tamisage; que la silice, l'alumine, l'acide phosphorique, sont constamment enlevés par la soude, et qu'on peut se débarrasser de la chaux et de la magnésie en traitant le peroxide de fer (préalablement lavé pour en extraire le sulfate de soude qu'il renferme) par un peu d'acide hydrochlorique extrêmement étendu. La pratique a montré qu'un peroxide de fer, renfermant même jusqu'à 40 degrés d'impuretés, continuait à fournir de très-bonnes sodes.

Cette même circonstance montre que, dans le nouveau procédé, il ne peut plus y avoir de perte d'alcali, quand même le sulfure de fer n'aurait pas été complètement épuisé, puisque la soude qu'on y laisse se retrouve, après la calcination du sulfure, à l'état de sulfate de soude dans le peroxide de fer et fait partie intégrante d'un nouveau bloc de soude brute ferrugineuse, préparé avec ce peroxide.

C'est même à la présence d'une quantité assez notable de soude, qui reste insoluble dans le sulfure de fer, que celui-ci doit la propriété de brûler avec tant de facilité et de fournir un peroxide très-fin, très-poreux et d'une nuance assez belle pour qu'on puisse parfaitement l'utiliser comme couleur, après en avoir extrait le sulfate de soude par un lavage à l'eau bouillante.

Il est évident qu'en faisant usage de peroxide de fer, renfer-



mant déjà du sulfate de soude, il faut considérablement changer les proportions du mélange pour la soude brute ferrugineuse. L'expérience a enseigné que le dosage le plus avantageux se rapprochait des proportions suivantes :

125 kilog. sulfate de soude.

140 kilog. peroxide de fer, provenant du sulfure.

70 à 75 kilog. charbon.

Et ces proportions sont ensuite conservées pour toutes les opérations subséquentes, aussi longtemps que dure la rotation du même oxide et sulfure de fer.

Ce n'est qu'en employant un peroxide de fer nouveau ou un peroxide épuisé par l'eau bouillante, qu'il faudrait adopter pour la première fabrication de la soude brute ferrugineuse les proportions indiquées au commencement.

En substituant au fer et à ses oxides le manganèse ou le zinc, on produit dans les mêmes circonstances des soudes brutes manganifères et zincifères, qui permettent également de fabriquer le sel de soude, tout en recouvrant le soufre ; mais l'expérimentation en grand a démontré que le manganèse et le zinc, outre qu'ils sont d'un prix plus élevé, ne présentent pas autant d'avantages dans la fabrication continue que le fer. C'est surtout l'opération de la délitation et de la carbonation qui présente certaines difficultés avec le manganèse et le zinc.

Avant de terminer cette notice, qu'il me soit encore permis de faire observer que ce nouveau procédé n'est pas fondé seulement sur des expérimentations positives et des analyses exactes faites dans le laboratoire, mais que depuis dix mois il est mis en pratique avec un succès complet dans un très-grand établissement, et qu'il a par conséquent déjà reçu la sanction de l'expérience.



ON  
AN APPARENT PERTURBATION  
OF THE  
LAW OF DEFINITE PROPORTIONS  
OBSERVED IN THE COMPOUNDS OF  
ZINC AND ANTIMONY.

By JOSIAH P. COOKE, JR., CAMBRIDGE.

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[Extracted from the *American Journal of Science and Arts*, 2nd Series, Vol. XX,
Sept. 1855; from a *Memoir of the American Academy*, New Series, vol. v, p. 337.]
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NEW HAVEN.  
PRINTED BY EZEKIEL HAYES.

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## ON AN APPARENT PERTURBATION, &c.

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IN a former paper in this Journal\* I described two new compounds of zinc and antimony  $\text{Sb Zn}_3$  and  $\text{Sb Zn}_2$  which I named respectively, Stibiotrizincyle and Stibiobizincyle, because they resemble in their composition the metallic radicals of organic chemistry, and because the first decomposes water rapidly at  $100^\circ \text{C}$ . I there stated that crystals of  $\text{Sb Zn}_3$  could be obtained containing a much larger amount of zinc than that required by the law of definite proportions, and that this change was not accompanied by any alteration of crystalline form. A similar variation of composition was afterwards observed in the crystals of  $\text{Sb Zn}_2$ , and it is the object of the present paper to describe the law of the variation in both cases and to explain its cause.

In the course of my investigations on this subject, crystallizations were made or attempted of alloys differing in composition by one half to five per cent., according to circumstances, from the alloy containing 95 per cent. of zinc to that containing 95 per cent. of antimony; but only two crystalline forms were observed, that of  $\text{Sb Zn}_3$  and that of  $\text{Sb Zn}_2$ . Well defined crystals, like those described under  $\text{Sb Zn}_2$  in the former paper,† were obtained from the alloys between 43 and 60 per cent. of zinc; and even in alloys of a higher zinc per-centage, crystals of the same form were still seen, although they were no longer well defined. In the alloys between 20 and 33 per cent. of zinc, well defined crystals, like those described under  $\text{Sb Zn}_2$  in the same paper, were formed; and finally there separated from the alloys between 33 and 42 per cent. of zinc thin metallic plates, which evidently belonged to the same crystalline form. In making the alloys from 43 to 95 per cent. of zinc, the zinc was melted first,

\* This Journal, vol. xviii, p. 234.

† Ibid.



and when in fusion the antimony was added. As the melting point of antimony is much above that of zinc, the fluid zinc acted on the solid antimony as a solvent, dissolving the pure metal, but not the impurities, which rose to the surface forming a scum. This scum seemed to take with it some of the antimony and thus caused a loss, which, together with the impurity, was found by experiment to be about three per cent. of the antimony used. This resulted in raising the per-centage of zinc in the alloy at most about eight-tenths of one per cent. The alloys below 43 per cent. of zinc were made by melting the antimony first, and then adding zinc. By this method the loss of antimony was very greatly diminished, and, counting the impurity, was found to be only about one per cent. and a half of the antimony used. In preparing the alloys this loss was always allowed for, and the crystallizations were all made as nearly as possible under the same circumstances, so that any unexpected cause of error should affect all equally. The crystals formed in the alloys were all analyzed in my laboratory under my direction and immediate supervision, and the greater part of them by myself. The rest were by my assistants, Mr. F. H. Storer, Mr. C. W. Eliot, and Mr. C. S. Homer, to whose care and accuracy I take pleasure in bearing witness. Their work is in all respects as reliable as my own. The results are collected in the following table which will explain itself.

*Analyses of the Crystals formed in the Alloys of Zinc and Antimony.*

| STIBIOTRIZINCYLE.                       |                |                                          |                |         |                      | STIBIOBIZINCYLE.                        |                |                                          |                |         |                      |
|-----------------------------------------|----------------|------------------------------------------|----------------|---------|----------------------|-----------------------------------------|----------------|------------------------------------------|----------------|---------|----------------------|
| Composition of the Alloys by Synthesis. |                | Composition of the Crystals by Analysis. |                |         | Name of the Analyst. | Composition of the Alloys by Synthesis. |                | Composition of the Crystals by Analysis. |                |         | Name of the Analyst. |
| Per ct. of Zn.                          | Per ct. of Sb. | Per ct. of Zn.                           | Per ct. of Sb. | Sum.    |                      | Per ct. of Zn.                          | Per ct. of Sb. | Per ct. of Zn.                           | Per ct. of Sb. | Sum.    |                      |
| 70.40                                   | 29.60          | 64.15                                    | 35.77          | 99.92   | Cooke.               | 33.00                                   | 67.00          | 35.37                                    | 64.57          | 99.94   | Cooke.               |
| 66.50                                   | 33.50          | 61.00                                    | 39.00          | *100.00 | Cooke.               | do.                                     | do.            | 35.40                                    | 64.60          | +100.00 | Cooke.               |
| 64.50                                   | 35.50          | 53.50                                    | 41.44          | 99.94   | Cooke.               | 32.50                                   | 67.50          | 34.62                                    | 64.92          | 99.54   | Storer               |
| • • •                                   | • • •          | 55.49                                    | 44.42          | 99.91   | Homer.               | do.                                     | do.            | 34.61                                    | 65.39          | +100.10 | Eliot.               |
| 60.60                                   | 39.40          | 55.00                                    | 45.09          | 100.09  | Homer.               | 31.50                                   | 68.50          | 33.95                                    | 66.09          | 100.04  | Storer.              |
| 58.60                                   | 41.40          | 50.39                                    | 49.29          | 99.68   | Eliot.               | 29.50                                   | 70.50          | 33.62                                    | 66.38          | +100.10 | Storer.              |
| 56.60                                   | 43.40          | 49.92                                    | 50.05          | 99.97   | Eliot.               | do.                                     | do.            | 23.62                                    | 66.38          | +100.00 | Storer.              |
| 54.70                                   | 45.30          | 48.26                                    | 51.42          | 99.68   | Storer.              | 27.50                                   | 72.50          | 33.85                                    | 65.81          | 99.66   | Storer.              |
| 52.70                                   | 47.30          | 47.47                                    | 52.53          | +100.00 | Cooke.               | 26.50                                   | 73.50          | 32.08                                    | 67.60          | 99.68   | Storer.              |
| • • •                                   | • • •          | • • •                                    | • • •          | • • •   | • • •                | 26.00                                   | 74.00          | 30.74                                    | 69.06          | 99.80   | Cooke.               |
| 50.70                                   | 49.30          | 46.89                                    | 53.11          | +100.00 | Cooke.               | 25.50                                   | 74.50          | 30.43                                    | 69.51          | 99.94   | Storer.              |
| do.                                     | do.            | 46.45                                    | 53.55          | +100.00 | Cooke.               | 25.00                                   | 75.00          | 29.88                                    | 70.20          | 100.08  | Cooke.               |
| 48.70                                   | 51.30          | 48.66                                    | 51.34          | +100.00 | Eliot.               | 24.50                                   | 75.50          | 28.76                                    | 71.24          | 100.00  | Cooke.               |
| 46.70                                   | 53.30          | 46.77                                    | 53.23          | +100.00 | Eliot.               | 23.50                                   | 76.50          | 27.93                                    | 71.85          | 99.78   | Cooke.               |
| 44.80                                   | 55.20          | 44.26                                    | 55.73          | +100.00 | Eliot.               | 22.50                                   | 77.50          | 26.62                                    | 73.27          | 99.89   | Storer.              |
| 43.80                                   | 56.20          | 44.04                                    | 55.96          | +100.00 | Cooke.               | 21.50                                   | 78.50          | 24.83                                    | 74.74          | 99.57   | Cooke.               |
| 42.80                                   | 58.20          | 43.15                                    | 56.83          | 100.08  | Cooke.               | 20.12                                   | 79.88          | 20.58                                    | 79.42          | 100.00  | Cooke.               |
| do.                                     | do.            | 43.06                                    | 56.50          | 99.56   | Cooke.               |                                         |                |                                          |                |         |                      |
| do.                                     | do.            | 42.83                                    | 57.24          | 100.07  | Cooke.               |                                         |                |                                          |                |         |                      |

\* In this analysis the antimony only was determined.

† In this analysis the zinc only was determined.

*Curve of Variation in Composition.*—In order to compare together the composition of the crystals and that of the alloy in which they form, I have resorted to the usual method of Analytical Geometry, and in the plate illustrating this paper, the lower horizontal line is the axis of abscissas, and the vertical line at the extreme left the axis of ordinates. The first has been divided into equal parts, which denote the per cents. of zinc in the crystals and the last into parts of the same size, which stand for the per cents. of zinc in the alloys. The zinc rather than the antimony determinations have been selected for comparison, as being generally more accurate, and as having been all made in exactly the same way. The points determined by analysis are indicated with dots, and the double line drawn through these dots is a curve, which represents the relation of the composition of the crystals to that of the alloy in which they form. In order to make clear the connection between the two, it will be well to discuss this curve, commencing with what may be termed the two centres of crystallization, the alloys of 42·8 and 31·5 per cents. of zinc, and examining the effect produced on the crystals by diminishing or increasing the amount of zinc in the alloy.

It has already been stated that the crystals of  $\text{Sb Zn}_3$  are obtained in their greatest perfection from the alloy of 42·8 p. c. of zinc. They are then comparatively large, generally aggregated, and, as the three analyses cited in the former paper prove, have the same composition as the alloy. On increasing gradually the amount of zinc in the alloy up to 48·7, the crystals continued to have the composition of the alloy, and the only difference, which could be observed in their character, was, that they were smaller and more frequently isolated. Between these limits, the whole mass of the alloy exhibited a strong tendency to crystallize, and, by pouring it, as it cooled, from one vessel to another, it could be crystallized to the last drop. The portion *a, b*, of the curve is therefore a straight line equally inclined to the two axes. On increasing the amount of zinc in the alloy to 50·7 p. c., the amount of zinc found in the crystals was only 46·89 p. c., and above this it was uniformly less than it was in the alloy; but no closer relation between the two could be detected, owing undoubtedly to the unavoidable irregularity in the crystallizations of the alloys, which contained more than 50 p. c. of zinc. This arose from a peculiar pasty condition, which the fluid mass assumed, at the point of crystallization, apparently caused by the separation of the excess of zinc. Definite crystals however were obtained even from the alloy of 60 p. c. of zinc, which contained 55 p. c.; above this, the crystals became less and less abundant, and gradually faded out, although the alloy even of 86 p. c. of

zinc exhibited a radiated crystalline texture ; and a trace of this structure could still be discovered even in the alloy containing only 4 p. c. of antimony. It might be supposed that on returning to the alloy of 42.8 p. c. of zinc, and increasing the amount of antimony we should obtain crystals containing an excess of antimony ; but so far is this from being true that the slightest excess of antimony entirely changes the character of the crystallization. On crystallizing an alloy containing 41.8 p. c. of zinc not a trace of any prismatic crystals could be seen, but in their place there was found a confused mass of thin metallic scales, which, as will soon be shown, are imperfect crystals of  $\text{Sb Zn}_2$ . Thus it appears that although perfectly formed crystals of  $\text{Sb Zn}_3$  can be obtained containing 55 p. c. of zinc they can not be made to take up the slightest excess of antimony.

In order to obtain crystals having the composition of  $\text{Sb Zn}_2$ , that is, containing 33.5 p. c. of zinc, it is necessary to crystallize an alloy at least as low as 31.5 p. c. of zinc. At this point large compound crystals are obtained corresponding to the large crystals of  $\text{Sb Zn}_3$ . On increasing the amount of zinc in the alloy up to 33 p. c., the proportion of zinc in the crystals appeared to increase in the same ratio, so that the curve of  $\text{Sb Zn}_2$  is at this part a straight line parallel to the curve of  $\text{Sb Zn}_3$ . It should however be noticed that the extent of this line *k i* is so limited that a very small error in the analyses might change very considerably its direction. The crystals of  $\text{Sb Zn}_2$  containing an excess of zinc, are smaller and more frequently isolated than those containing exactly two equivalents. A similar fact, it will be remembered, is true of the crystals of  $\text{Sb Zn}_3$ . At the alloy of 33 p. c. of zinc, the definite crystals of  $\text{Sb Zn}_2$  begin to disappear and are succeeded by thin metallic scales, which, as the two following facts will prove, are imperfect crystals of the same crystalline form. First, the scales from the alloy of 23 p. c. are frequently found having a definite crystal as a nucleus, when it is evident that their surfaces are extensions of the basal plane O of fig. 2 of the former memoir. Secondly, the scales twin together like the large tabular crystals of  $\text{Sb Zn}_2$ , forming a cellular structure, and the angle between two scales thus united, measured with an application goniometer approximately  $115^\circ 30'$ , and was therefore equal to the basal angle of the definite crystals. These scales continue up to the alloy of 41.8 p. c. of zinc, becoming however constantly less abundant and less distinct. Several specimens of them were analyzed, but no regularity in their composition could be detected except that they all contained a very much larger amount of zinc than the alloys in which they formed. This irregularity and the imperfection in the crystallization seem to be caused by the interference of  $\text{Sb Zn}_3$ , that is, by a tendency to form  $\text{Sb Zn}_3$  which exhibits itself in a proneness of the crystals of  $\text{Sb Zn}_2$  to



an excess of zinc. The line *k i* has been continued with dots in order to show that the influence of  $\text{Sb Zn}_2$  extends as far as the alloy of 42.8 p. c. of zinc. On returning to the alloy of 31.5 p. c. of zinc and adding an excess of antimony it was found that the crystals formed continued to have the theoretical composition of  $\text{Sb Zn}_2$  until the amount of zinc in the alloy had fallen to 27 p. c., so that the tendency towards the theoretical composition was so great, that in the alloys between 31.5 and 27 p. c. of zinc, crystals were formed having very nearly this composition. On still further increasing the amount of antimony in the alloy, the composition of the crystals gradually approached that of the alloy, and from the alloy of 20.2 p. c. of zinc, very imperfect crystals were obtained having almost the same composition as the menstruum. At the same time, the crystals became less and less perfect and finally disappeared altogether in the alloys below 20 p. c. of zinc.

The portion of the curve *k m n h*, is the most important result of this investigation and therefore deserves especial notice. It has been shown that crystals of the form of  $\text{Sb Zn}_2$ , or at least crystalline scales of the same character, are formed in the alloys between 20 and 43 p. c. of zinc, the first per cent. corresponding to  $\text{Sb Zn}$  and the second to  $\text{Sb Zn}_3$ . Half way between these two points, that is the alloy of 31.5 p. c., is the point where crystals having the calculated composition of  $\text{Sb Zn}_2$  are first obtained. Were the variations in the composition of the crystals of  $\text{Sb Zn}_2$  exactly proportioned to the excess of zinc or of antimony in the alloy, as is the case with  $\text{Sb Zn}_3$ , then the curve of variation would be the straight line formed by the continuation of the line *a b*. From this line *b h* the course of the curve is deflected by the force which determines the union of the elements in definite proportions, and which for the want of a special term, I will call the Chemical Force. This is so strong that the curve runs parallel to the axis of ordinates through the distance *k m*. Beyond this point, the influence of the excess of antimony in the alloy becomes stronger than the chemical force, and the curve gradually bends towards the line *h b* which it finally meets at *h*. In the portion *h n* of the curve, the analyses are best represented by the arc of a circle, of which the radius equals *h e* or one-half of *h b*, and to which the line *k m* is tangent. In the portion *n m* the points determined by analysis may also be connected by the arc of a circle of which the radius *o' n* equals the difference between the radius *o n* and twice *g n*, so that the two centres are at the same distance from the line *a h*. The whole curve is evidently the result of two forces; one acting along the chord in the direction *b h*, a force tending to increase the amount of antimony in the crystals proportional to the amount in the alloy, the same force in fact, which acts undisturbed in forming the portion of the curve *b a*; the other the chemical force acting in the di-



rection of the tangent  $km$ . It has already been stated that crystals having the calculated composition of  $\text{Sb Zn}_2$  are not first formed in the alloy of the same composition 33·5 p. c. of zinc, but in an alloy containing two per cent. less; so that the line  $mk$ , instead of extending to  $e$ , changes from this direction at  $k$ , and afterwards runs parallel to the line  $bh$ . Unless this fact can be explained by a tendency in  $\text{Sb Zn}_2$  to an excess of zinc caused by the influence of  $\text{Sb Zn}_3$  as suggested above, the reason of this difference between  $\text{Sb Zn}_2$  and  $\text{Sb Zn}_3$  in this respect is not clear; but as some evidence that it is not accidental it may be stated, that the distance  $kc$  equals  $ci$ , the last point being the one, at which the tangent line  $mk$  extended meets the curve. Another remarkable fact whose bearing cannot be at present seen, but which like the last serves to corroborate the general accuracy of the result was pointed out by my colleague, Prof. Peirce, after the plate had been engraved. The distances of the three most important points of the curve of  $\text{Sb Zn}_2$  from the line  $ah$ , viz.  $kd$ ,  $mf$ , and  $ng$ , are simple multiples of the first;  $ng$  is twice and  $mf$  three times  $kd$ . The curve has been fixed, as will be noticed from the dots, by a large number of points determined throughout the greater part of its length at every per cent., and in the portion  $mn$  at every half per cent.; they certainly coincide with the curve as closely as could possibly be expected, and the very agreement of so many different determinations by three separate analysts is a strong proof of the general correctness of the work.

By making hypotheses in regard to the nature of the two forces, which have generated the curve just described, it would not be difficult to obtain for it a mathematical expression; but as such hypotheses, in our ignorance of the nature of these forces, would be premature, I must content myself with giving its geometrical construction on a chart ruled like the plate illustrating the memoir. Let the coördinates of any point of the curve be,  $x$  = per cent. of zinc in the crystals, and  $z$  = per cent. of zinc in the alloy. In order to construct the curve of  $\text{Sb Zn}_3$ , find a point ( $a$ ) of which  $x = z = 43$  p. c. (the calculated per cent. of  $\text{Sb Zn}_3$ ) and draw a straight line  $ab$  equally inclined to the two axes in the direction from the origin. To construct the curve of  $\text{Sb Zn}_2$ , produce the line  $ab$  in the opposite direction to the point  $x = z = 20$ , which will be the lowest point of the curve. Find next a point ( $k$ ) of which  $x = 33\cdot7$  p. c. (the calculated per cent. of  $\text{Sb Zn}_2$  is 33·5) and  $z = 31\cdot5$  p. c., which is one-half of  $43 + 20$ . Through this point draw a line  $mk$  parallel to the axis of ordinates and intersecting the line  $abh$  at  $c$ . The line  $mi$  is the tangent, and the line  $bh$  the chord of the required arc. On the line  $mi$  take  $ci = ck$ , and  $i$  is the point at which the arc should touch the tangent. Erect a perpendicular on the tangent at the point  $i$ , take  $oi = \frac{1}{2} bh$ , and from  $o$  as a centre, with a ra-

dius =  $o i$ , describe the arc  $h i$ . Also from the centre  $o$  let fall a perpendicular  $o g$  on the chord  $b h$ , and produce it to a point  $o'$  making  $o' g = o g$ . It will intersect the arc at  $(n)$ . From  $o'$  as a centre with a radius  $o' n$  describe a second arc  $n m$  intersecting the tangent at  $m$ . Finally, draw from  $k$ , a straight line  $k l$ , parallel to  $b h$ , then the broken line  $l k m n h$  will be the required curve.

It will be noticed that the tangent which has been drawn on the plate through the points determined by analysis is two-tenths of a per cent. in advance of the line which would correspond to  $\text{Sb Zn}_2$ . This position is essential to the equality of  $k c$  and  $c i$ , if we retain as the value of the radius of the larger arc  $R = \frac{1}{2} b h$ . If the analyses should have given erroneously too much zinc so that the true position of the line should be at  $x = 33.5$  per cent., then this equality would be destroyed, and the conditions for finding the centre  $o$  would be reduced to the coördinates of the point  $h$ , the length of the radius and the position of the tangent, from which by a very simple construction the curve might be drawn. It should however be remarked that the position of the tangent in advance of the line  $x = 33.5$  is in accordance with the fact, already noticed, that the crystals of  $\text{Sb Zn}_2$  have throughout a proneness to an excess of zinc caused apparently by the influence of  $\text{Sb Zn}_3$ ; but it is also true that the tendency of the error in the zinc determinations is in the same direction.

Before discussing the conclusions to which the facts already stated seem directly to point, it will be well to see how far the variation in composition corresponds to a variation in the properties of the two compounds. Three classes of properties have been examined in this connection, viz., Specific Gravity, Crystal-line Form, and Affinity for Oxygen, which will be treated of in order.

*Specific Gravity.*—The specific gravities of all the crystals analyzed, as well as that of the zinc and antimony used in the investigation, were taken with the greatest care. The determinations were made with a nicely constructed specific gravity bottle, as this method was found susceptible of greater accuracy than any other, when the temperature was observed with precision. In calculating the specific gravity, the weight of the water was corrected for the temperature, so that the unit is in all cases distilled water at  $4^\circ \text{C}$ . A similar correction could not be made for the temperature of the substance, as the coefficients of expansion of the crystals are not known. The results of the determination all made by myself are collected in the following table in the column headed "Sp. Gr. by Experiment." In the column headed "Mean Sp. Gr. of Zinc and Antimony" are given the cal-

*Specific Gravities of Crystals, formed in the Alloys of Zinc and Antimony.*

| Composition of the Alloys. |                | Composition of the Crystals |                | Sp. Gr. of Crystals by Experiment. | Mean Sp. Gr. of Zinc and Antimony. | Expansion in Crystallizing. |
|----------------------------|----------------|-----------------------------|----------------|------------------------------------|------------------------------------|-----------------------------|
| Per ct. of Zn.             | Per ct. of Sb. | Per ct. of Zn               | Per ct. of Sb. |                                    |                                    |                             |
| 100.00                     |                |                             |                | 7.153                              | 7.153                              | 0.000                       |
| *96.00                     | 4.00           |                             |                | 7.069                              | 7.134                              | 0.065                       |
| *86.20                     | 13.80          |                             |                | 6.898                              | 7.086                              | 0.188                       |
| *76.30                     | 23.70          |                             |                | 6.769                              | 7.039                              | 0.270                       |
| 70.40                      | 29.60          | 64.20                       | 35.80          | 6.699                              | 6.982                              | 0.283                       |
| 66.50                      | 33.50          | 61.00                       | 39.00          | 6.628                              | 6.967                              | 0.339                       |
| 64.50                      | 35.50          | 58.56                       | 41.44          | 6.596                              | 6.956                              | 0.360                       |
| 62.50                      | 37.50          | 55.53                       | 44.47          | 6.506                              | 6.941                              | 0.435                       |
| 60.60                      | 39.40          | 55.00                       | 45.00          | 6.440                              | 6.939                              | 0.499                       |
| 58.60                      | 41.40          | 50.39                       | 49.61          | 6.396                              | 6.917                              | 0.521                       |
| 56.60                      | 43.40          | 49.95                       | 50.05          | 6.388                              | 6.915                              | 0.527                       |
| 48.70                      | 51.30          | 48.66                       | 51.34          | 6.404                              | 6.909                              | 0.505                       |
| 46.70                      | 53.30          | 46.77                       | 53.23          | 6.376                              | 6.900                              | 0.524                       |
| 44.80                      | 55.20          | 44.26                       | 55.74          | 6.341                              | 6.888                              | 0.547                       |
| 42.80                      | 57.20          | 43.09                       | 56.91          | 6.327                              | 6.882                              | 0.555                       |
| *40.00                     | 60.00          |                             |                | 6.386                              | 6.867                              | 0.481                       |
| *35.00                     | 65.00          |                             |                | 6.404                              | 6.844                              | 0.440                       |
| 33.00                      | 67.00          | 35.37                       | 64.63          | 6.401                              | 6.845                              | 0.444                       |
| 29.50                      | 70.50          | 33.62                       | 66.38          | 6.384                              | 6.837                              | 0.453                       |
| 27.50                      | 72.50          | 33.85                       | 66.15          | 6.383                              | 6.838                              | 0.455                       |
| 26.50                      | 73.50          | 32.08                       | 67.92          | 6.400                              | 6.829                              | 0.429                       |
| 26.00                      | 74.00          | 31.07                       | 68.93          | 6.418                              | 6.824                              | 0.406                       |
| 25.50                      | 74.50          | 30.43                       | 69.57          | 6.428                              | 6.822                              | 0.394                       |
| 24.50                      | 75.50          | 28.76                       | 71.24          | 6.449                              | 6.813                              | 0.364                       |
| 22.50                      | 77.50          | 26.62                       | 73.38          | 6.453                              | 6.803                              | 0.350                       |
| 21.50                      | 78.50          | 24.83                       | 75.17          | 6.467                              | 6.795                              | 0.328                       |
| *15.00                     | 85.00          |                             |                | 6.564                              | 6.748                              | 0.184                       |
| *10.00                     | 90.00          |                             |                | 6.603                              | 6.725                              | 0.122                       |
| *5.00                      | 95.00          |                             |                | 6.655                              | 6.701                              | 0.046                       |
|                            | 100.00         |                             |                | 6.677                              | 6.677                              | 0.000                       |

culated specific gravities of the same crystals on the supposition that the two metals had undergone no expansion on uniting. The last column was obtained by subtracting the numbers of the former from those of the latter, and therefore shows the relative amount of expansion. On examining the table, it will be found 1st. That the union of antimony and zinc is accompanied by expansion. 2nd. That the specific gravity of the crystals varies slightly with the composition. 3d. That the two minimum specific gravities correspond precisely to the composition of  $\text{Sb Zn}_2$  and  $\text{Sb Zn}_3$ , so that the specific gravity increases and the expansion diminishes as you depart on either side from these two centres. 4th. That the specific gravity of  $\text{Sb Zn}_3$  is smaller than that of  $\text{Sb Zn}_2$ . We find then that the specific gravity determinations confirm in general the results of the analysis pointing out the same two centres of crystallization.

*Crystalline Form.*—It has already been stated that only two crystalline forms can be obtained from the alloys of zinc and antimony, that of  $\text{Sb Zn}_3$  and that of  $\text{Sb Zn}_2$ . A large number of

\* Alloys not crystallized.



crystals of  $\text{Sb Zn}_3$  from different alloys, and therefore containing different proportions of zinc, were carefully measured for the purpose of ascertaining whether the angle was at all affected by the variation of composition. Fortunately four different crystallizations afforded excellent crystals, the angles of which could be measured to a minute. The crystals contained respectively 43.15, 44.14, 46.90 and 55.00 per cents. of zinc, and on all these by repeated measurements the angles were found to be *identical* with those given under figs. 1 and 2. Crystals from many of the other alloys were also measured, but on account of the imperfections of their surfaces the angles could not be determined within five or ten minutes. In all these cases however the values of the angles given above were included within the limits of uncertainty.

The faces of the crystals of  $\text{Sb Zn}_2$  are not generally so perfect as those of  $\text{Sb Zn}_3$ , nor is their tabular form so well adapted for measurement; moreover variations in some of the angles have been noticed in crystals from the same crystallization amounting even to ten minutes. The angle 0 on 1 however appeared to be very constant for in all cases where it could be accurately measured the same value was obtained. As none of the crystals of  $\text{Sb Zn}_2$ , containing an excess of antimony, could be measured with precision, no constant variation of angle could be detected and on the other hand it could not be proved to be invariable.

*Affinity for Oxygen.*—The affinity of the crystals of  $\text{Sb Zn}_3$ , of different compositions, for oxygen, may be estimated by comparing the amounts of hydrogen gas evolved in a given time on boiling alloys of the same composition with water. The results of such experiments were given in the former memoir in a table, a mere glance at which will discover the two following facts—

1st, That up to 40 per cent no great increase in the amount of hydrogen evolved is obtained by increasing the amount of zinc in the alloy.

2nd, That at the alloy containing 42 per cent. of zinc there is an immense maximum confined at most between two per cent on either side.

*General Conclusions.*—Before stating the conclusions to which as I think the facts now established directly point, it will be well to consider the only two admitted principles of chemical science which could possibly be brought forward to explain similar variations. They are, first, that of impurities in crystals; second, that of isomorphous mixtures. It will not be difficult to show that the variations in composition of  $\text{Sb Zn}_2$  and  $\text{Sb Zn}_3$  cannot be caused by either of these principles.

It is a well known fact that crystals frequently take up impurities which are either dissolved or mechanically suspended in the

menstruum in which they form, and it might be supposed at first sight that the excess of zinc or antimony in  $\text{Sb Zn}_3$  or  $\text{Sb Zn}_2$ , bore the same relation to their crystals that the sand does to the rhombohedron of calcite from Fontainebleau, or oxyd of iron and chlorite to crystals of quartz; but, in the first place, in all cases where a considerable amount of impurity is present the crystals are either imperfect or else the angle is considerably changed at times even as much as two or three degrees; and secondly, as such impurities are merely mechanical, the amount in the crystals would in all probability be proportional to the amount present in the menstruum at the time of their formation. Now in the crystals of  $\text{Sb Zn}_3$ , from the alloy of 60 p. c. of zinc, there is present an excess of zinc amounting to 15 p. c. and nevertheless the crystals are as perfect as, and their angles identical with, those obtained from the alloy of 43 per cent. In the crystals of  $\text{Sb Zn}_3$  the excess of zinc is to a certain limit directly proportional to the excess in the alloy, but in those of  $\text{Sb Zn}_2$  the excess of antimony is far from obeying this rule; and were the excess in both cases a mechanical mixture the variation in both cases would undoubtedly follow the same law: again, the crystals of  $\text{Sb Zn}_3$ , take up an excess of zinc but do not take up an excess of antimony, while those of  $\text{Sb Zn}_2$  crystallize with an excess of either, —facts which are as inconsistent with the idea of mechanical impurity as the last: finally the form of the curve of  $\text{Sb Zn}_2$  of itself alone proves that the excess of antimony in the crystals is not in the condition of mechanical impurity; for in that case the variation of composition would not be influenced, as the curve shows that it is, by the chemical force.

A theory that the variation in composition resulted from the mixture of two or more isomorphous compounds would be even less tenable than the one just discussed. For in the first place it would be necessary to assume the existence of two other compounds of zinc and antimony isomorphous with  $\text{Sb Zn}_2$  and of one other, if not more, isomorphous with  $\text{Sb Zn}_3$ . Not only would such an assumption be contrary to all the analogies of chemistry and therefore require strong evidence to sustain it; but in the second place it can almost be demonstrated that no such compounds exist. The crystals having the calculated composition of either  $\text{Sb Zn}_3$  or  $\text{Sb Zn}_2$  are marked as has been shown by striking peculiarities, and with one possible exception similar peculiarities were not observed throughout the whole series of crystals which have been examined. The crystals containing 50 per ct. of zinc and of the composition of  $\text{Sb Zn}_4$  were found to have a slightly smaller sp. gr., than those just above or just below them, but the difference is so small that it may be accidental, and as the crystals exhibited none of the other peculiarities, which characterize crystals having the calculated composition of  $\text{Sb Zn}_3$  or

$\text{Sb Zn}_2$ , I could not attach sufficient weight to the one circumstance to feel authorized in admitting a third compound of zinc and antimony. Admitting however the existence of  $\text{Sb Zn}_4$  yet, as exactly the same angle has been observed in crystals containing 55 per cent. as on those containing 43 per cent of zinc, it would be necessary in order to explain the variation in composition by the principle of isomorphous mixtures, to assume the existence of still a third compound isomorphous with  $\text{Sb Zn}_3$ , and containing more zinc than  $\text{Sb Zn}_4$ , which would increase greatly the improbability of the theory in question. Again, the only probable compound of zinc and antimony containing less zinc than  $\text{Sb Zn}_2$  would be  $\text{Sb Zn}$ ; and it will be remembered that the crystals of  $\text{Sb Zn}_2$  which contained the largest excess of antimony corresponded very nearly to this compound. In like manner the crystals of  $\text{Sb Zn}_2$  which contained the largest excess of zinc corresponded very nearly to  $\text{Sb Zn}_3$ . If then the excess of antimony or zinc in the crystals of  $\text{Sb Zn}_2$ , arises from a mixture of isomorphous compounds, it must be that  $\text{Sb Zn}_3$ ,  $\text{Sb Zn}_2$  and  $\text{Sb Zn}$  are isomorphous. That the first two are not isomorphous may be seen by turning back to the description of their crystalline form; and that there is no crystalline compound  $\text{Sb Zn}$  is sufficiently proved by the fact that the crystals of  $\text{Sb Zn}_2$ , which correspond most closely to it, are so very imperfect that they would hardly be recognized as crystals did they not form the lower limit of a series. Several other facts pointing in the same direction might be added, but sufficient it is thought has been said to show that the variations of composition described in this paper can not be explained either by mechanical impurities in the crystals or by the mixture of isomorphous compounds.

In the absence of any known principle of chemical science by which the remarkable variations of composition, that have been demonstrated in this memoir, can be explained, the conclusion is almost forced upon us that zinc and antimony are capable of uniting and producing definite crystalline forms in other proportions than those of their chemical equivalents: in other words, that the law of definite proportions is not so absolute as has been hitherto supposed. The explanation then of the variation of composition which I would offer is: that it is due to an actual perturbation of the law of definite proportions produced by the influence of mass. I suppose for example that in the crystals of  $\text{Sb Zn}_3$ , containing 55 per cent. of zinc, the zinc and antimony are united in exactly the same way as in those containing 43 per cent., or in other words, just as if the equivalent of zinc were increased to 52.57, that of antimony remaining the same. In support of this position I would offer two considerations. The first is that if the variation is not caused by mechanical impurities or by the mixture of isomorphous compounds, we can conceive of no other explana-



tion for the phenomenon than the one offered. This of course is merely negative evidence; for although science as yet presents us with no principle for explaining variations of composition other than those which have been discussed, and although we can conceive of none others, it does not follow that others may not exist or may not hereafter be discovered; but, nevertheless, this consideration is important inasmuch as it meets an obvious objection, which would be urged against any new doctrine, which conflicts with a generally received canon of chemical philosophy. The second consideration has the character of demonstration. It is that the curve of variation is evidently generated by a second force counteracting directly the chemical force. This second force, as has been shown, is exerted by the excess of one or the other element present in the menstruum, and it may therefore be appropriately termed the force of mass. While the chemical force tends to make the curve a straight line parallel to the axis of ordinates, the force of mass would reduce it to a straight line making an angle of  $45^\circ$  with the axis; under the influence of both these forces it follows the arc of a circle between the two. Now I urge that the character of this curve proves that the chemical force has been directly influenced by what we have called, the force of mass, in the same way that the irregularities of the orbits of the planets prove that the force of gravitation exerted by the sun has been disturbed in its action by the influence of the other members of the system. As the details in the form of the curve have been fully discussed in the previous part of the memoir, it does not seem to be necessary to dwell upon this argument, and I would therefore without further comment offer the curve as it has been laid down on the plate as the proof of the validity of the explanation of the variation in composition here advanced.

It is worthy of remark that while the curve of variation may be said almost to demonstrate that the law of definite proportions may be disturbed in its action, it also most clearly sustains the integrity of the law itself; for, as may be seen on inspection, the chemical force is sufficiently strong to retain the curve of  $\text{Sb Zn}_2$  parallel to the axis of ordinates through a variation in the menstruum of nearly five per cent., and it is only when the excess of antimony present in the alloy exceeds six per cent. that the force which it exerts becomes strong enough to disturb the action of the law. What the nature of the disturbing force is must be for the present a matter of theory. I am inclined to think that it is a phase of the chemical force itself, in the same way that the perturbations in the motions of the planets are a secondary result of the force of gravitation.

Accepting the view of the subject, which has been offered, it will be obvious that the very large extent of the variation in the

compounds of zinc and antimony is due to the very weak affinity between these elements. Were the chemical force stronger in proportion to the disturbing force the variation would be lessened; were it weaker, the variation would be increased. This is illustrated in the difference between the curve of  $\text{Sb Zn}_3$  and that of  $\text{Sb Zn}_2$ . It is evident from the action of chemical agents on the two compounds, that one equivalent of antimony and two of zinc are united by a stronger force than one equivalent of antimony and three of zinc, and we find that the crystals of  $\text{Sb Zn}_2$  retain the calculated composition under a considerable variation in the composition of the menstruum, while the composition of those of  $\text{Sb Zn}_3$  varies with the slightest increase of the amount of zinc in the alloy.

To what extent this perturbation of the law of definite proportions prevails among chemical compounds it must remain for future investigation to determine. There are however a number of facts which tend to prove that it is very general whenever chemical affinity is weak. Four of these I will cite as being remarkably analogous to the facts under discussion.

1. Rieffel, to whose investigation of the compounds of tin and copper we have already referred, says, after the paragraph quoted in the introduction to this memoir, "*Les aiguilles de  $\text{CuSn}_{2.4}$  sont plus grosses que celles de  $\text{CuSn}_{4.8}$* ". "*On croit, sans oser l'affirmer, qu'elles sont, par compensation, en nombre moindre, et que des différences analogues ont lieu dans les autres  $\text{CuSn}_\varphi$  à mesure que  $\varphi$  augmente jusqu' à  $\varphi=\infty$ , ou jusqu' à l'étain pur.*" It will be noticed that the difference between these needles is precisely the same as the difference between the crystals of  $\text{Sb Zn}_3$  containing a small and a large amount of zinc, and I think that no one after reading Rieffel's paper can doubt that the compounds of copper and tin vary in composition like those of zinc and antimony.

2. The mineral Discrasite, a compound of silver and antimony, crystallizes in trimetric prisms, of which  $I$  on  $I=119^\circ 59'$ .\* The analyses given below are copied from Dana's System of Mineralogy, changing slightly the order.

$\text{Sb Ag}_3 = \text{Antimony } 28.5 \text{ Silver, } 71.5=100.$   $\text{Sb Ag}_4 = \text{Antimony } 23, \text{ Silver } 77=100.$

|                                     |          |       |        |                           |
|-------------------------------------|----------|-------|--------|---------------------------|
| 1. Andreasberg (foliated granular), | Antimony | 24.25 | Silver | 75.25=99.5, <i>Abich.</i> |
| 2. Wolfach (coarse granular),       | "        | 24    | "      | 76=100, <i>Klaproth.</i>  |
| 3. Andreasberg (foliated granular), | "        | 23    | "      | 77=100, "                 |
| 4. " " " "                          | "        | 22    | "      | 78=100, <i>Vauquelin.</i> |
| 5. Wolfach (fine granular),         | "        | 16    | "      | 84=100, <i>Klaproth.</i>  |

It needs no comment on these results to show that Discrasite is homœomorphous with  $\text{Sb Zn}_3$ , and varies like it in composition.

\* Dana's System of Mineralogy, 4th ed., vol. ii, p. 35.

3. In a paper recently published,\* W. Sartorius von Waltershausen gives descriptions and then analyses of a new mineral occurring with Dufrenoy'site in the Binnen Valley, Switzerland, in Dolomite. As the analyses do not agree with each other and do not correspond to a simple formula, von Waltershausen regards the compound as consisting of two hypothetical isomorphous compounds  $\text{Pb S} + \text{As S}_3$  and  $2\text{Pb S} + \text{As S}_3$  and calculates the proportions in which these compounds are mixed in the specimens analyzed. He infers that they are isomorphous from their analogy in composition to Zinkenite and Heteromorphite,  $\text{Pb S} + \text{Sb S}_3$  and  $2\text{Pb S} + \text{Sb S}_3$  which he regards as isomorphous. Prof. J. D. Dana questions the isomorphism of the last and thinks that the hypothesis that the new compounds are isomorphous requires further evidence.†

4. It is stated by Staedeler‡ that crystals of the compound of grape sugar and common salt can be obtained containing for every equivalent of grape sugar one or two equivalents of chlorid of sodium and also of intermediate composition. He states moreover that "Calloud, who first observed that the grape sugar of honey combined with chlorid of sodium, found that the amount of the latter varied between 8.3 and 25 per cent." Staedeler refers the variation in composition to a mixture of the compound of one with the compound of two equivalents of chlorid of sodium which he assumes to be isomorphous. He adds that it may be caused by "enclosed crystals of chlorid of sodium although the eye could not distinguish any heterogeneous constituents."

All the above compounds are examples of weak chemical affinity accompanied by large variations in composition without any change in the general crystalline form. It is not meant to assert that the variations are identical in character with those of  $\text{Sb Zn}_3$  and  $\text{Sb Zn}_2$ , but only that there is a strong probability that this is the case, which in the first two instances amounts almost to a certainty.

If variations in composition of such magnitude are possible when the force of chemical affinity is weak, it is highly probable that some variation may occur when the force is strong, and, whatever view may be taken of the cause of the variation it will now become a matter of importance to ascertain whether many discrepancies in analyses hitherto referred to imperfections in the process, may not be owing to the same cause which influences the composition of the crystals of zinc and antimony. For this purpose, it will be best to make several analyses of the same compound, prepared under circumstances differing as widely as possible, and then to apply to the results "Peirce's Criterion for

\* Poggendorff's *Annalen*, vol. xciv, p. 115.

† *American Journ. of Science*, vol. xix, p. 355.

‡ *Chemical Gazette*, vol. xiii, p. 44.



the rejection of doubtful observations." Such investigations will be greatly simplified by tables prepared by Dr. B. A. Gould\* for facilitating the application of this criterion to which I would refer all chemists who are inclined to take up this line of investigation.

I am well aware that in announcing the existence of perturbations of the law of definite proportions I am calling in question one of the most fundamental dogmas of chemical philosophy, and that the new doctrine will have to encounter prejudice on this very ground. This law is so intimately associated in many minds with the atomic theory, that, to such, absolute definiteness seems to be its essential characteristic; nevertheless, I can not but believe that, laying aside the prejudices which the theory begets, it will be seen by all, that the analogies of nature support the doctrine of variation as maintained in this memoir. The phenomena of some of the phenomenal† laws of nature have that definiteness of character which is claimed for those of the chemical law. The planetary orbits are not perfect ellipses. The ratios of the harmony scale are but approximately realized. The arrangement of leaves on the stem is not perfectly regular. Isomorphism is seldom absolute. In all we observe only a tendency towards a maximum effect which is the perfect expression of the law, but which is rarely fully reached. The limits of variation are broader in some instances than in others, but we find no case in which there is absolutely none. This same character which pervades the other phenomenal laws of nature, I claim for the great law of chemistry. The definite proportion I regard as a maximum toward which the chemical force strives, a maximum, from which the deviations in most cases are small, although in others it may be very large; and I maintain that this view of the subject, which the memoir has aimed to establish, is supported by the analogies of nature.

When the dynamical law has been discovered, of which the phenomenal law was merely the outward manifestation, as Kepler's laws were merely the phenomena of the law of universal gravitation, the very variations have been seen to be necessary consequences of the law itself, and if even the dynamical law, which governs chemical phenomena, shall be discovered, it is most probable that the variations from the law of definite proportions will become as much a matter of calculation as the perturbations of Astronomy. In both cases the perturbation is apparently due to the influence of an extraneous mass of matter.

\* *Astronomical Journal*, vol. iv, p. 81.

† I have used the term phenomenal laws to designate a class of laws of nature which are empirical in their character inasmuch as they are obviously not ultimate, although their deviation has not been discovered, but which are more universal than those to which the term empirical is commonly applied.

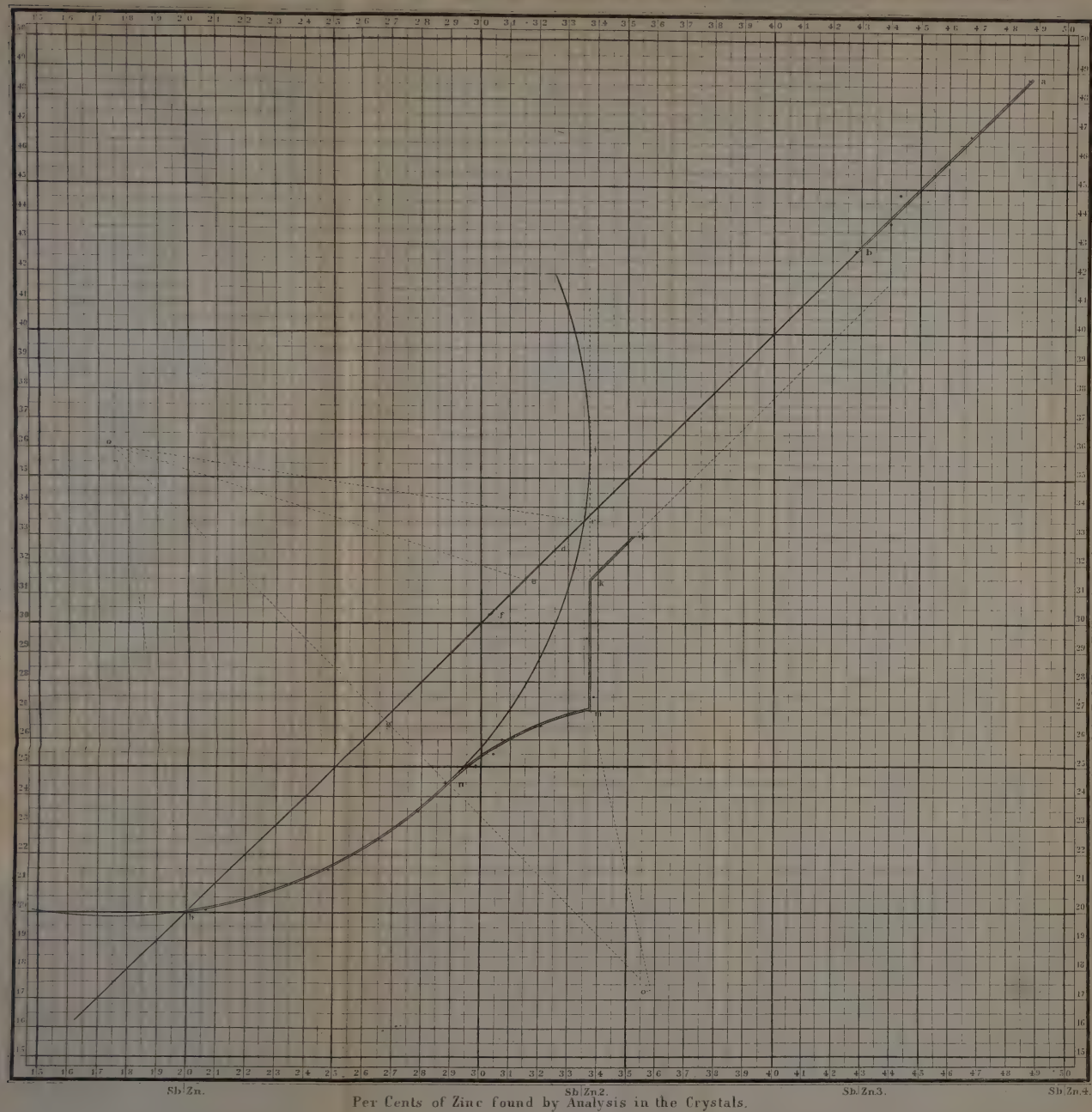
The argument from analogy becomes stronger, when we consider the equivalent numbers. I have shown in a former memoir\* that these numbers may be connected by a very simple numerical law, but here, as in other cases, we find merely a tendency towards the law, not an absolute agreement with it, the differences between the theoretical and the experimental equivalents being in many cases too great to be covered by errors of observation. The present memoir may throw light upon these discrepancies; for, to say the least, it is possible that the differences may originate in variations of the equivalent itself, and that the theoretical equivalent may be the maximum towards which the chemical force tends. On comparing carefully the different determinations of the chemical equivalents, many facts may be noticed supporting this view; those equivalents for example, which coincide with or very nearly approach whole numbers such as those of oxygen, carbon and sulphur, will be found as a general rule to have been determined by the analysis or synthesis of compounds whose elements are united by a strong force; also when the equivalents have been determined by essentially different processes it will be noticed that they seldom perfectly agree; so that whatever view may be taken of the subject it will now become a matter of the highest importance to ascertain how far, if at all, the determinations of the chemical equivalents have been influenced by similar causes to those which have produced the variations described in this memoir. This influence can only be detected by multiplying the determinations, by as many different processes as possible, and submitting the results to a rigorous mathematical scrutiny.

If the doctrine of this memoir is correct and the chemical equivalents are really liable to variation it will have an important influence on chemical philosophy. The atomic theory as at present interpreted by chemists is irreconcilable with it, and our present ideas in regard to isomorphism must be materially changed. But it must be remembered that the conclusions of the memoir are drawn from the examination of only two compounds, and therefore that it would be premature to dwell on these obvious consequences of the principle until it has been substantiated by further investigations. In conclusion, I would express my obligation to the gentlemen who have assisted me in the labor of the investigation which on account of the large number of analyses has been very great and could not have been concluded so soon had it not been for their great industry and zeal.

\* This Journal, vol. xviii, p. 229,

CURVE EXHIBITING THE VARIATION IN COMPOSITION OF THE CRYSTALS FORMED IN THE ALLOYS OF ZINC AND ANTIMONY.

Per Cents of Zinc in the melted Alloys in which the crystals were formed.



Per Cents of Zinc found by Analysis in the Crystals.





REVIEW OF Dr. ANTISELL'S WORK ON PHOTOGENIC OILS, &c.

[The following Review of Dr. Antisell's book on Photogenic Oils has been for some months in type waiting an opportunity when our other engagements would permit its publication. It will amply repay the careful perusal of all who are interested in this important practical subject.—EDS.]

REVIEW.

1. *The Manufacture of Photogenic or Hydro-Carbon Oils from Coal and other Bituminous Substances capable of supplying Burning Fluids*; by THOMAS ANTISELL, M.D., Professor of Chemistry in the Medical Department of Georgetown College, D. C., etc. etc. New York and London: D. Appleton & Co. 1859. pp. 144.—In entering an earnest protest against the work before us, we would not have our motives misunderstood. We are not of those who would condemn a book solely on the ground that it is "not so good as it should be," and will not therefore urge this objection against the effort of our Author, although it would be hard to find a case to which the charge would more forcibly apply. But we do condemn most heartily the presumption of the man who in these days attempts to write a handbook upon any scientific or technological subject with which he is not somewhat familiar. We believe, moreover, that errors, either of omission or of commission—accidental or intentional—in scientific writings, which exceed the well-understood conventional limits of *tolerance*, should not be allowed quietly to pass without correction.

Dr. ANTISELL, from his position of chemical examiner in the Patent Office at Washington, has naturally had a rare opportunity of familiarising himself with the recent improvements which have been made—or claimed—in the manufacture of coal oils. In the work in question, he has published an index of these, which cannot but be acceptable to all who are interested either in the practical or scientific consideration of the subject. Had this list been published by itself, or had it been incorporated with a portion of the materials which Dr. A. has now exhibited, in an article, or a short series of articles, in some one of our scientific or technological magazines, it would have been most gratefully received, and, we doubt not, widely copied. Diluted and scattered as this information has been, however, that it might fill a volume, its value has been lessened in no slight degree.

We have endeavored, in vain, to make out the point of view from which the Author regarded his subject. Claiming the attention of all persons engaged in the manufacture of liquid products from the distillation of mineral combustibles, his work is nevertheless not a didactic one. In it scarcely any attempt is made to instruct the manufacturer, either by a clear enunciation of general principles to be followed, or of special details to be observed in given cases;\* while a most lamentable lack of familiarity with the chemistry of the subject is continually exhibited throughout the work. Indeed the book is simply a jumble of badly selected extracts, huddled together in a manner which must be anything but edifying to the student. As a compilation, it has the merit of directing attention to a number of sources from which valuable information may be derived; while it has the great fault of omitting to mention numerous other sources of knowledge of equal or of greater value.

In several instances, moreover, erroneous assertions are made, or wrongful conclusions drawn. One or two of these we propose to discuss and correct

\* In this respect our author has fallen far below the level attained by previous writers upon the subject. Compare for example: UHLENBUTH, *Handbuch der Photogen-und Paraffin-Fabrikation*. Quedlinburg Basse, 1858.

in this article. Our attention will be especially directed to the first chapter of Dr. Antisell's book—"History of the Art"—for in it are errors which have too long been current in the annals of chemical science—errors, the repetition of which by our author is the more unpardonable, since, from his very position, he should have known them to be such. Indeed, from statements to be found in various parts of his work, it would appear that he must have known of these errors—that he must have been in possession of most of the facts which will here be brought forward.

That we may form a correct notion of the subject under discussion, let us here digress for a moment.

As a general rule, when any bituminous substance is subjected to distillation—in the ordinary acceptance of the term, *i. e.*, when it is gradually heated in any appropriate apparatus, a quantity of an oily fluid is produced, which may be collected in receivers; small quantities of gas, water, and other incidental products being at the same time obtained.

The oily liquid, which alone interests us here, known in this country as *crude coal oil*, is a mixture of various hydrocarbons, among which the wax-like substance Paraffine is an almost never-failing constituent. Crude oil, though of course varying greatly, according to the sources from which it is derived, like the various marketable "coal oils" obtained from it by purification, is specially characterized by its low specific gravity, being capable of floating upon water.

When, on the other hand, a bituminous substance, instead of being gently and gradually heated, is suddenly exposed to the action of an intense heat—when, as in the ordinary process of gas-making, it is thrown into vessels of iron or clay, which have *previously* been brought to a bright red heat, a different set of products is obtained. A large quantity of permanent gas is produced, while the liquids formed are no longer the light oily compounds just spoken of, but are composed of another set of hydrocarbons which taken collectively, are *heavier than water*. These constitute coal-tar. Among them paraffine is no longer found, excepting in comparatively rare instances, another solid substance, Naphthaline, being a characteristic component of the mixture. When the process to which the bituminous matter is subjected is a mixed one, *i. e.*, when a portion of the substance comes in contact with strongly heated surfaces, while other portions receive only an amount of heat sufficient to distill off oils of the kind first described, a mixed product, containing both coal-oil and coal-tar, is naturally obtained. As an instance of such mixed product may be mentioned the tar obtained in the preparation of gas from Boghead coal,\* it being almost impossible, in this case, to maintain the retorts at the temperature best suited for gas-making, on account of the great amount of heat which is rendered latent by the enormous volume of gas generated by this highly bituminous substance.

It should be mentioned, that both crude coal-oil and coal-tar contain a quantity of "light stuff" composed of several exceedingly volatile and inflammable liquids. Some of these naphtha-like fluids, for example benzol—the benzine of the French—(known as *benzole* in the private vocabulary of Dr. Antisell, or that of his proof-reader)—may occur both in crude-oil and in tar; others do not. We refer to these "light-stuffs" here merely for the purpose of explaining that they have been at times spoken of as "volatile oils," from the resemblance which they bear to spirits of turpentine and other essential oils, and to eliminate them from the discussion. They are of but minor interest at the present moment, when compared with the true "coal-oil" now so largely employed in this country. We may mention, in passing, that Dr. Antisell has very inconsiderately obscured his historical sketch of the progress of the art of distilling coal-oil

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\* In the same class are several Scotch cannels, our own Breckenridge and allied coals, also the Albert coal of New Brunswick and the like.



by blending with it the question of coal-tar naphthas. He has, for that matter, been unfortunate throughout in the presentation of this part of his subject; all the crude liquid products of distillation, at whatever temperature the process has been conducted, being indiscriminately classed by him as *tar*. Now, it is well known to practical men, as has already been described, that the products obtained from bituminous matters by slowly distilling them, is as different from coal-tar as ether is from alcohol. The term crude-oil, by which the first-named liquid is known to manufacturers in this country, characterizes it perfectly; so does the term *huile de schiste* (written at times simply "*schiste*") of the French.\*

It is surprising that Dr. Antisell should have followed the example of several German authors—without their excuse—in thus perplexing his readers.

In returning from this digression, we would expressly declare our disbelief in the adage which allows for the existence of no novelty. Still we do believe that very few of the arts have sprung into existence in a day, their perfection, and especially their development, having almost always resulted from the successive labors of numerous individuals; and we do believe that the inventor, who first practically "applies" any abstract knowledge, and thus creates a new art or branch of industry, is entitled to credit therefore—and to far more credit, and that of a different order, than the man who subsequently introduces this art into a foreign country. We would not detract from the efforts of the latter; on the contrary, would accord them high praise; but we desire, first of all, to see justice meted out to him who created the art—to those who increase human knowledge, sooner than to its mere diffusers.†

We would therefore join issue with Dr. Antisell when, in his preface, he tells us that his book is a "record of the origin and condition of an infant art," and again mentions "this new branch of industry." So, also, in the first lines of his Historical Introduction, where he speaks of "the new and extensive manufacture of oils from coal and other bituminous substances." For these statements are not only erroneous in themselves, but they—no less than the unfair allusions which appear on subsequent pages—tend to do great injustice to earlier inventors, and especially to the memory of a man whose name must ever remain inseparably connected with the history of the *art of manufacturing the fluid now known as coal or paraffine-oil*. We refer to SEL-LIGUE. More than twenty-five years ago, this inventor's method of obtaining such oil was described in the *Journal des Connaissances Usuelles*, for Dec., 1834, p. 285. (See also *Dingler's Polytechnisches Journal*, 1835, lvi, 40.) This article was subsequently followed by numerous others, until in Selligue's patent of March 19, 1845, we find the whole subject treated of most fully and clearly. As a lucid and truthful description of his processes and of the products obtained, this specification is most praiseworthy. Few subsequent writers upon the subject have been able to add anything to the stock of knowledge which it imparts. Taken for all in all, it is doubtless the most meritorious essay which has ever been published upon the art of manufacturing coal-oil. We can but reiterate our statement, that the brief, inaccurate, and exceedingly superficial comments which have been bestowed by Dr. A. (pp. 9, 80, etc.) upon the information which Selligue has imparted in his admirable series of essays, does great injustice to the subject as well as to this author.

Leaving for a moment the minute consideration of Selligue's improvements, let us first glance at the labors of some of his predecessors.

As Dr. Antisell has truly said (p. 7), the discovery of the production of oil from coal appears to date as far back as the time of Boyle, (1728–1759), when the well known experiments of Dr. Clayton were made.‡

\* We may here observe, that throughout this article we shall translate the French term *huile de schiste*, by its English equivalent, *coal-oil*.

† Philosophical Transactions, Jan. 1729, No. 452, p. 69; in Martyn's Abridgment, vol. ix. p. 395.

In distilling coal from a pit near Wigan in Lancashire, this observer obtained, first phlegm (water), then oil, and finally gas.

No doubt an earlier record of similar experiments might be found in the writings of the alchemists, who, as is well known, subjected almost every substance to processes of distillation.

During the last century attention was again several times called to the fact.\*

It would seem, however, that nothing very definite was published before the year 1830. UNVERDORBENT† had, indeed, in the preceding year, called attention to oils distilled from petroleum, and even appears to have obtained paraffine—to which however he gave no name.‡ The attention of the scientific world was first really attracted to this substance by the memorable memoir of Reichenbach,§ who separated it, in the first instance, from wood tar, and described its properties at length. In the following year, Reichenbach|| is at great pains to prove that the crude-oil, obtained by slowly distilling coal, contains no naphthaline,¶ that naphthaline is not a product of the slow distillation of coal, but is a result of the subsequent decomposition of such products by heat; and that the coal-tar of gas-works is not crude-oil, but an impure mixture of the products of distillation with those resulting from their decomposition.\*\*

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\* In addition to the authorities cited by Dr. A. (p. 8), we would mention the following from *An Experimental History of the Materia Medica, or of the Natural and Artificial Substances made use of in Medicine*; by WILLIAM LEWIS M.B., F.R.S., 3rd Edit. 8vo, Dublin, MDCCCLXIX, vol. ii, p. 143. Article *Petroleum*; also, (according to American Druggists' Circular, iv, 36,) in the London edition of Lewis. 4to, 1761, p. 436:

"Some mineral oils, procurable among ourselves, are used by the common people, and often with benefit. The empirical medicine, called British oil, is of the same nature with the petrolea; the genuine sort being extracted by distillation from a hard bitumen, or a kind of stone coal, found in Shropshire and other parts of England."

† *Berzelius's Jahresbericht*, x, 181, from *Kastner's Archiv*, xvi, 122; also in *Schweigger-Seidel's Journal für Chemie und Physik*, 1829, lviii, 243.

‡ For allusions to other earlier German researches bearing upon the subject, see Reichenbach's Memoirs, which will be cited directly. Compare also Gmelin's *Handbook of Chemistry* (Cavendish Soc. Edit.), xii, 439.

§ *Journal für Chemie und Physik*, (or *Jahrbuch der Chemie u. Physik*, Band, xxix) von Schweigger-Seidel, 1830, lix, 436.

|| *Ibid.* (or *Neues Jahrbuch der Chemie u. Physik*, B. 1,) lxi, 175.

¶ Dr. Antisell dismisses this article (p. 11) with the statement that "in 1830-'31, Reichenbach discovered naphthalin." It may not be amiss to state that naphthaline was discovered at least ten years earlier, having been described by GARDEN in 1820 (*Thomson's Annals of Philosophy*, xv, 74), to whose labors as well as to those of CHAMBERLAIN, KIDD, and others, Reichenbach particularly refers in this very article. See also *loc. cit.* B. lxviii, [B. viii, of the "*Neues Jahrbuch*,"] S. 233.

\*\* It must here be explained that Reichenbach has suffered great injustice at the hands of those who, in translating portions of his papers, have rendered his term "*Steinkohlentheer*" literally—coal-tar. Now the term coal-tar, in countries abounding in gas-works like England or the United States, means the tar of gas-works, and it means nothing else. Gas-works, it must be remembered, were, until quite recently, by no means so common in Germany, and were doubtless rare enough in 1830, consequently, it is not at all strange that the English idea of "coal-tar" should not have become current in that country. Reichenbach, for that matter, distinctly and repeatedly asserts, that his "*Steinkohlentheer*" is a very different substance from the tar of gas-works. In a word, it was *crude-oil*. If, perchance, there may be any person who would accuse us of mistranslating certain words used by Reichenbach, we would at once refer such an one to the original memoirs of this author. Submitting it to the judgment of any competent chemist, whether we have misinterpreted his lan-

These experiments were made upon a manufacturing scale, Reichenbach being, at this time, "chief of an extensive system of mines, iron furnaces, machine shops, chemical works, etc., most of them established by himself on the estate of Count Salm [Blankso, Moravia]. These works lie along a line some fifteen miles [5 *Stunden*] in length." (Schweigger Seidel).

In another article published later, in 1831,\* he describes his method of obtaining paraffine from the distillation of flesh and of coal (portions of 75 lbs. weight having been operated upon). With regard to coal, he particularly urges the necessity of slow distillation, in order to prevent the decomposition of the first products and the consequent formation of naphthaline, as explained in his previous article, to which he refers. The paraffine was separated from the less volatile portions of the rectified oil by cooling—the description of which oil R. reserves for a separate article.† He also obtained paraffine from petroleum. Two more papers upon the subject were published by Reichenbach in this year,‡ only the first of which is of particular importance in this connection. It relates to *Eupion* (εὔ very, πίων fat). A term by which Reichenbach designates, in some instances, a portion, in others the whole of the somewhat difficultly volatile, fat-like oils, prepared by purifying the first product obtained by slowly distilling substances of animal or vegetable origin. This eupion was, in fact, a mixture of several hydrocarbons—the same which, in similar mixtures, are now collectively known in commerce as coal-oil; called paraffine oil by some, and designated in the retail trade by innumerable other names of only local significance.

Eupion was obtained by Reichenbach from the products of the slow distillation of animal and vegetable substances, as well as from coal, and was minutely described by him. We make but a single extract from this article, which occupies some thirty-two pages: "When any one shall succeed in separating eupion, at a sufficiently cheap rate, from the tars [crude-oils], it will very probably enter into the circle of substances useful in household economy. For, since it burns from a wick, brightly and clearly, and is free from smoke, it is in no wise inferior to the finest oil as an illuminating material. It does not grease nor crust the wick, nor stiffen when cold. If we consider, in addition to this, that for all purposes where cold can exert no influence, the paraffine need not be separated, but can be left dissolved in the eupion, and used in conjunction with it for lighting; we shall perceive that this is of some importance, since the two substances are thus mutually improved for technical purposes."

In 1832, Reichenbach§ again published a note upon eupion; and, in 1834, another long article,|| in which he once more dwells upon its useful properties.

Reichenbach's contributions on the subject of the dry distillation of organic substances, are comprised in some twenty or more long articles, not counting

guage, [compare, for example, *loc. cit.*, B. lxviii., [B. viii. of the *Neues-Jahrbuch.*,] S. 226].

It may be worth while also to call the attention of the reader to the fact that all of the substances discovered by Reichenbach in "tar" (as the text-books tell us) were in reality obtained from crude-oil. Knowing this, every one familiar with recent chemical literature, will perceive at once why so few of R.'s scientific results have been corroborated. For, until quite recently, the attention of chemists interested in such researches, has been almost completely occupied with the subject of coal-tar. Compare also Reichenbach's complaint against Dumas and Laurent, in Schweigger-Seidel's *Journal für Ch. u. Phys.*, 1838, lxviii., 223.

\* *Loc. cit.*, lxi, [or B. 1, of the *Neues-Jahrbuch*], S. 273.

† *Vid. infra.*

‡ *Loc. cit.*, lxii, [or B. ii. of the *Neues-Jahrbuch*], S. 129, 273.

§ *Loc. cit.*, B. lxvi, [B. vi. of the *Neues-Jahrbuch*], S. 318.

|| Erdmann's *Journal für praktische Chemie*, i, 377.



several smaller "notes." A tolerably complete list of which may be found in Edmann's *Journal für praktische Chemie*, i, 1. It is very much to be regretted that these memoirs have never been collected and published as a separate volume. Even now, any chemist who could find time to collect these scattered articles and translate them into English or French, would unquestionably promote the cause of science by so doing.

Looking at the question for a moment, solely in its scientific bearings, we cannot refrain from an expression of astonishment, that the details of Reichenbach's researches are so little known to the generality of chemists;\* while, on the other hand, we are forced to confess, that it is indeed rare that scientific researches, conducted by a chemist in his laboratory, have so fully described a future art—have so accurately pointed out the methods to be followed and precautions to be observed by the practical manufacturer. We must not omit to mention that, in 1831, Christison† of Edinburgh made known his discovery of paraffine in petroleum from Rangoon. Not knowing of Reichenbach's previous publication, Christison named it *Petroline*, but subsequently admitted its identity with paraffine. In 1833, Bley‡ distilled oils from lignite.

A little later, in 1834, Gregory§ published an able article upon paraffine and eupion, and their occurrence in petroleum. Of this memoir we cite but two lines, (vid. *Trans.*, p. 129, or *Rep.*, p. 113). "It follows," says Gregory, "that there are some kinds of naphtha [petroleum] which contain paraffine and eupion, and are consequently the results of destructive distillation."

In the following year, v. Kobell|| also noticed paraffine in petroleum.

For the labors of Hess in Russia, and of several other chemists in Germany, as well as for the interesting discussions which followed between these

\* This lack of information appears to depend upon the circumstance, that the writers of most recent chemical text-books seem to have derived their knowledge of the subject in question, from Gay Lussac's brief abstract of Reichenbach's earlier memoirs, which was published in 1832, in Poggendorff's *Annalen*, xxiv, 173; also in the *Annales de Chimie et de Physique*, [2], 1, 69; and quite extensively copied by the journals of the day.

In this connection we would respectfully urge upon all those who have fallen into the common habit of regarding as somewhat apocryphal the numerous substances of greater or less scientific interest, which Reichenbach separated from the products of dry distillation, that before seeking to discredit—or allowing themselves to disbelieve—they, they should conduct experiments similar to his, *on a scale of equal magnitude*. Let us here also bear in mind the luminous conclusion of the late Dr. Hore of Edinburgh, who, as the story goes, (Vid. *London Chemical News*, i, 56), one day informed his class that Reichenbach had discovered in tar, "creosote, picamar, paraffine, cedriret, capnomor, and a host of other substances of no interest or importance whatever." Of these "unimportant" substances, two at least, eupion and paraffine, are to-day as well known, in the world, as bees-wax or spermaceti, although comparatively little—we had almost said nothing—has been added to the scientific knowledge of them, since the publication of Reichenbach's memoirs. If, perchance, any other of these well-nigh forgotten bodies should be found to possess any technical importance, we would quickly enough find some one claiming credit for its "discovery," and oppressing chemical nomenclature, by adding yet another name to the existing "host." Even now we await, with no little interest, the elucidation of the question—whether the new violet dye, prepared by oxydizing anilin, which is exciting so much interest, under the names anilein, Perkin's purple, *mauve*, etc., is not identical with, or a component of, the *pittical* of Reichenbach.

† Transactions of Royal Society of Edinburgh, xiii, 118; also in *Repertory of Patent Inventions*, 1835, [N. S.] vol. iii, p. 390.

‡ Schweigger-Seidel's *Journal für Chemie u. Physik*, B. lxi, [B. ix, of the *Neues Jahrbuch*], S. 129.

§ Transactions of Royal Society of Edinburgh, xiii, 124; also in *Repertory of Patent Inventions* 1835, [N. S.] vol. iv, p. 109.

|| J. pr. Chem. v. 213.

observers and Reichenbach, the reader may consult the general index [Namen-u. Sach-Register zu den Bänden i. bis lx, Leipzig, 1845] to Poggen-dorff's *Annalen der Physik u. Chemie*.

At the same time that these scientific researches were in progress in Germany and Scotland, or even earlier, numerous practical efforts to manufacture oils from bituminous substances were made in France.

Although the precise date at which these experiments were commenced is somewhat obscure, it will not be difficult to trace the history of the successful development of the industry to which they gave rise.

As stated by Dr. Antisell, the MM. Chervan\* had a patent, dated in 1824, for distilling bituminous substances. Blum and Moneuse,† in 1832, claim only the application of coal-oil to purposes of lighting—not its manufacture, which they allude to as being well known.

Subsequently (7th October, 1833) Boscary‡ obtained a patent for extracting pyrogenous oil from different substances, asphaltums, etc., and especially from the shales which occur in the environs of Autun (*Saône et Loire*), and finally from all the bituminous matters in France. The oil, which is obtained by distilling the shale in metallic cylinders, may be used, according to Boscary, instead of fish-oil or resin, for gas-making—a much better gas than that prepared from coal being thus obtained.

In 1833, Laurent§ occupied himself with the investigation of various bituminous shales, both French and English, at the instance of the MM. Blum, whom he mentions as being occupied with the distillation of oil from the shales of the environs of Autun || Laurent gives the details of the process employed by himself, telling us that the retort in which his shales were distilled attained a sombre red heat at the close of the operation; also of the percentage amounts of oil (20 p. c.), gas, coke and water obtained from the Autun shale; how the oil cannot be burned in ordinary lamps, on account of smoking, but affords a very luminous flame when consumed in lamps furnished with suitable chimneys. He shows moreover that the oil contains paraffine, and does not contain naphthaline.

Laurent subsequently published another paper¶ upon this oil, in which article he records his efforts to ascertain what definite chemical compounds are contained in the oil. One of the products obtained by fractional distillation, viz., an oil boiling at  $167^{\circ}$  to  $170^{\circ}$  (C.) =  $333^{\circ}$  to  $338^{\circ}$  F., he considers as identical with eupion.

In 1834, we find, for the first time, an article\*\* describing the process of Selligie, although it would appear from the statements of this chemist and of others, that his attention had been directed to the subject of distilling bituminous shales several years earlier. The cited article relates how the shale is *slowly* distilled in iron cylinders, until no more oil comes over; how the oil obtained is characterized by containing neither oxygen nor naphthaline, but a solid substance differing from the latter, and resembling that called parannaphthaline†† by Laurent.

\* Brevets d'Invention xviii, 232.

† *Ibid.* lxx. 250.

‡ *Ibid.* lxxviii, 359.

§ *Annales de Chimie et de Physique*, liv, 392.

|| According to Laurent, he had himself proposed to a company, in 1829, to work these shales, in order to extract the oil contained in them, and to employ it for lighting.

¶ *Comptes Rendus*, 1837, iv, 909; more fully in *Annales de Chimie et de Physique*, lxxiv, 321.

\*\* *Journal des Connaissances Usuelles*, Dec. 1834, p. 285; also in Dingler's *Polymisches Journal*, 1835, lvi, 40, from which our extract is taken.

†† The inadvertency of confounding this body with paraffine was subsequently corrected by Selligie.

In 1834, '35 and '36, Selligie\* was principally occupied with his well-known process for making water-gas. In calling the attention of the French Academy† to this, he remarks that, in conjunction with David Blum, he holds a patent granted in 1832 for the application of oils obtained from shale to purposes of direct illumination, and that the working of the shale employed is in the hands of a company capable of developing the business to any extent which commerce or the arts may require.

In the same year Payen,‡ in reporting upon Selligie's water-gas, remarks upon the great importance of the new industry of distilling oil from shales which S. has introduced.

In the following year we again find Selligie before the Academy§ requesting that body to appoint a committee to examine the merits of his new system of gas-lighting; his process of distilling bituminous shales on the great scale by means of apparatus, each one of which furnishes from 1,000 to 1,400 pounds of crude oil per day—this being about 10 per cent of the weight of the shale employed, and being almost all which exists in the raw material; also of his process of separating various products from the crude oil, some of which are applicable to the production of gas, others to ordinary purposes of illumination, and others to different uses in the arts. This petition was referred to a committee of three—Thenard, D'Arcet and Dumas—who reported in 1840.¶ They mention the localities of Selligie's three establishments for obtaining oil from shales; the amounts of oil obtained from the different kinds of shale, &c.

In 1838 Selligie also obtained a new patent|| “for the employment of mineral oils for lighting.” In his specification he informs us that the principles upon which his processes for rendering the oil obtained from shales proper for the purposes of direct\*\* illumination depend, are:

I. Removal of almost all odor. II. Removal of all tar. III. Removal of the most volatile portions of the oil, which are also the most inflammable and the most odorous, the presence of which would cause the oil to have too great fluidity for the capillarity of ordinary wicks. \* \* \*

The operations, continues Selligie, consist in slowly distilling the bituminous shale, and collecting the liquid products in large receivers. These products are redistilled, and divided into fractions by refrigerating. They are treated with concentrated sulphuric acid for a longer or shorter time according to the nature of the shale employed. Twenty-four hours are ordinarily sufficient, the oil being agitated from time to time. The quantity of acid used varies from  $\frac{1}{10}$  to  $\frac{1}{20}$ . After this the oil is to be carefully drawn off from the tar, and washed with water. Slaked lime is then added and a current of steam passed through the oil in order to carry off by distillation all the more volatile and odorous liquids. This last, says Selligie, is the most important part of my process, for if this very inflammable portion were allowed to remain in the oil, one could not use the latter in ordinary lamps à courant d'air. \* \* \* This patent it should be observed claims only to be an improvement upon that of Blum and Moneuse (*vid. Supra*). Selligie asserts, however, that coal-oil had never before been prepared in such a manner that

\* See seven patents in *Brevets d'Invention*, lxx, 269. Of these patents two are dated 1834; two, 1835; and three, 1836. For a description of his process of gas-making see also *Bulletin de la Société d'Encouragement*, Oct. 1838, p. 396; or *Dingler's Polytechnisches Journal*, lxxi, 29.

† *Comptes Rendus*, 1837, iv, 969.

‡ *Dingler's Polytechnisches Journal*, lxxviii, 201; from *Bulletin de la Société d'Encouragement*, Dec. 1837, p. 493.

§ *Comptes Rendus*, 1838, vii, 897.

|| *Comptes Rendus*, x, 861; also in *Dingler's Polytechnisches Journal*, lxxvii, 137.

¶ *Brevets d'Invention*, lxxviii, 395.

\*\* The term “direct illumination” is constantly used by Selligie in contradistinction to the indirect use of the oil in his process of gas-making.



it was fit for use in common lamps. This has, indeed, he says, been the subject of many researches, but no one has hitherto succeeded in avoiding the empyreumatic odor, and the very inflammable products which caused the oil to rise too quickly to the summit of the wick. He goes on to define the difference between his purified oil and the crude oil obtained directly from shale. On the 27th of March, 1839, Selligie specifies certain additions and improvements to the preceding patent. I should add, he says, that I now divide the products of distillation into four distinct parts, which afford me every facility for employing these products in the arts and for domestic economy. In these divisions there are indeed some anomalies which arise from differences in the shales, &c. which I treat; but the following products are always obtained:

I. A light, volatile oil more or less odorous according to the source from which it is derived. \* \* \* This can be used in painting, for dissolving resins, &c., for lighting by vaporising it (it being very volatile) or for the production of gas according to my system.

II. A fat oil only slightly volatile, and having but little odor; this can be used for domestic purposes in ordinary lamps with or without admixture of animal or vegetable oils.

III. A fatty substance almost odorless, possessing all the properties of the fats, and well adapted for use in the arts. It can also be used for lighting, either by mixing it with light oils or by decomposing it for the production of gas. It can moreover be used for soap\* since it saponifies very well, and being without odor affords a very good soap; with ammonia the fat forms a sort of pomade.

IV. An odorless pitch of great purity and tenacity, suitable for preparing a black solid varnish for preserving wood, iron-work, &c. \* \* \*

In 1839, Selliguet† in alluding to the use of his oils in the treatment of cutaneous diseases speaks of the three large establishments for the distillation of bituminous shale which he has erected in the Department Saone et Loire, and mentions the fact that the oil (crude?) is furnished at the rate of about two cents [ten centimes] per pound.

The question of price is again discussed a few years later, when Selliguet‡ says: it has been stated that crude shale oil costs only \$1 50 per 100 pounds, and that it contains 60 per cent of a very light volatile ethereal oil well suited to afford light, as well as 40 per cent of a fat substance. Now since 1837, I have extracted more than 4,000,000 pounds of oil from bituminous shale, but the oil (crude?) costs 20 cents a gallon (22 frs. the hectolitre) or even 27 cents when delivered in Paris. From every hundred measures of the crude oil are obtained (by distillation) 20 measures of volatile oil boiling at 100° C.=212° F.; 30 measures of less volatile oil boiling at 150° to 260° C.=302° to 500° F.; 14 measures of an oil containing paraffine, and 28 measures of fat—five measures being lost. In purifying these products a further portion is lost.

The clearest of all Selliguet's specifications, however, is that of the patent granted to him March 19, 1845§ for the distillation of bituminous shales and sandstones.

After describing the various forms of apparatus used in distilling, into one of which superheated steam was introduced, he enumerates the products of distillation as follows: I. A white, almost odorless, very limpid mineral oil—somewhat soluble in alcohol—which may be used as a solvent, or for purposes of illumination in suitable lamps, &c.

\* This "soap," (emulsion) is described more fully in the sequel.

† *Comptes Rendus*, ix, 140; also *Annalen der Pharmacie*, von Wöhler u. Liebig, xxxii, 123.

‡ Dingle's *Polytechnisches Journal*, xci, 193; from the *Moniteur Industriel*, 1843, No. 770.

§ *Brevets d'Invention*, [new series, (loi, du 5 Juillet, 1844,)] iv, 30.

II. A sparingly volatile mineral oil of sp. gr. 0.84 to 0.87, of a light lemon color, perfectly limpid, almost odorless, never becoming rancid, and susceptible of being burned in ordinary oil lamps, of constant level *à reservoir supérieur*, with double current of air—a slight modification of the form of the chimney and burner being alone necessary. This oil can also be mixed with the animal or vegetable oils. Oils thus prepared do not readily become rancid, nor do they congeal easily when subjected to cold.

III. A fat mineral oil, liquid at the same temperature as olive oil. This oil contains a little paraffine; it is peculiarly well adapted for lubricating machinery, and has an advantage over olive and other vegetable oils, or neats-foot oil in that it preserves its unctuousity when in contact with metals and does not dry up. It saponifies easily, and forms several compounds with ammonia.

IV. From the oils Nos. I, II, and III, I extract a red coloring matter which can be used in various arts.

V. White crystalline paraffine which needs but little treatment in order to be fit for making candles; this substance does not occur in very large proportion in the crude oil, and the proportion varies according to the different mineral substances upon which I operate. There is but little of it in petroleum, and in the oil obtained from bituminous limestone. I often leave a great part of the paraffine in the fat oil and in the grease in order that these may be of superior quality.

VI. Grease. This grease is superior to that of animals for lubricating machinery, and for many other purposes, since it does not become rancid, and remains unctuous when in contact with metals.

VII. Perfectly black pitch—very “drying”—suitable for preserving wood, metals, &c.

VIII. An alkaline soap obtained by treating the oils with alkalies.

IX. Sulphate of ammonia. X. Manure prepared by mixing the ammoniacal liquor, or the blood of animals, with the crushed fixed residue (coke) of the shale. XI. Sulphate of alumina from the residue of the shale. F. H. S.

In describing the methods of purification proposed by Selligie, we shall make no attempt to follow their various details, our limited space compelling us to content ourselves with only the broadest generalities. Selligie sets forth at length two methods: 1st. A cold treatment which consists in agitating the oil with sulphuric, muriatic, or nitric acid. This agitation should be thorough, he says, and should be continued for a longer or shorter time according to the nature and quantity of the matter treated. Here follows a description of his agitators. After several hours' repose, the oil may be decanted, except from muriatic acid in which case more time and a larger amount of acid is required. After the oil has been thus separated from the deposit of tar, the acid remaining in it must be neutralized by means of an alkali. I prefer, says Selligie, to employ the lye of soap-boilers marking 36° to 38° [B. 2], since it is easy of application, and produces a sure effect; I thus precipitate together the coloring matter and tar which would otherwise have remained in the oil. The oil is then decanted: if it is the first distillation of the crude oil I do not allow the mixture to subside entirely, preferring to leave a portion of the alkali mixed with the oil, and to distil off only  $\frac{1}{2}$ ths of the latter. \* \* \* When the soda lye—in quantity slightly greater than is necessary to neutralize the acid—is added, the liquid must be agitated violently in order that each particle of the oil may be brought in contact with the alkali; this agitation must be continued until the color of the oil undergoes change.

The oil becomes less odorous and less highly colored after each such “cold treatment.”

After having been allowed to separate from the lye, the oil is decanted off; if it has not lost much of its color the process has been badly conducted. It



should be stated that the oil must not be agitated several times with the alkali, for, by so doing, the dark color of the oil would be restored. \* \* \* As for the residues of the soda treatment, continues Selligie, they should be allowed to stand at rest during some days beneath a portion of oil, which will protect them from contact with the air; the clear lye at the bottom being then drawn off may be used for other operations, while the remainder is a soap, containing excess of alkali. By adding to it a little grease a soap can be made, or by adding water, grease may be separated. This grease is similar to that used for wagons.

2d. A warm treatment which follows the cold, and consists of a series of fractional distillations,—special operations for the purification of the “light-stuffs,” being resorted to. For the details of these we must refer to the original specification of Selligie—a truly classical document which should be read by every one interested in the manufacture of coal-oils.\* Nor will our limited space permit us to cite the detailed “example” of his treatment which Selligie has described. We trust that we have already written enough to enable the reader to judge whether or no Selligie understood his business.

As for paraffine, Selligie obtained it by subjecting the oil to a low temperature in order that this substance might crystallize. The mixed oil and paraffine was then thrown upon fine metallic filters through which the oil flowed while the paraffine was separated. Or one may separate, he says, the oil by imbibition, but this occasions a great loss of oil and also requires more labor. \* \* With this specification the scientific discussion of the subject by Selligie appears to have ceased, yet in the same year he replied† to a note published by Chenot‡ who asserted that the oil of shale often contains arsenic, denying that arsenic can be found in the products from his own establishments. He again describes the locality and geological position of his shale, the method of distillation employed,—how the temperature is gradually elevated, &c.

This is of interest as showing that the manufacture of coal-oil in France was no ephemeral fancy, but for many years was a well established branch of industry. In this connection the scientific research, upon the commercial products of the distillation of bituminous shale, of Saint-Evre§ should also be mentioned. Contemporaneous with Selligie we find other inventors occupied with the same subject. Thus Holthorp|| in 1841, claims that he has first discovered a means of purifying the fluid substance, which he calls “schiste,” resulting from the distillation of coal or of bitumen. His attention was evidently chiefly devoted to the volatile naphthas, but he also obtained paraffine.

Guillard Meynier,¶ in 1842, speaks of the fixed oil from shale, telling us that it may be used for lighting or lubricating and that paraffine may be separated when the oil is cooled or treated with alcohol.

In the same year Bonnet\*\* in treating of liquids suitable for lighting incidentally mentions eupion and paraffine.

Nor should we omit to mention the very interesting article upon *Hydrocarbures Liquides*, by A. Mallet (in Laboulaye's *Dictionnaire des Arts et Manufactures*, 2d Ed., Paris, 1854††), in which Selligie's processes are incidentally described. After discussing in detail the light volatile products obtained by distilling coal-tar, he says, we have still to speak of the carbo-hydrogens from shales; a branch of industry which we owe entirely to Selligie—cut off,

\* A tolerably accurate English translation of this important patent may be found in the specification of M. A. B. B. Du Buisson, 1845; specification No. 10,726 of the English Patent Office.

† *Comptes Rendus*, 1845, xx, 573.

§ *Comptes Rendus*, 1849, xxix, 339.

¶ *Brevets d'Invention*, lxxviii, 91.

‡ *Ibid*, xx, 306.

|| *Brevets d'Invention*, liii, 263.

\*\* *Ibid*, lxxix, 63.

†† A portion of this article, which directly refers for the most part only to the volatile products suitable for “burning fluids,” which may be obtained in any way from coal, is also contained in Dingler's *Polytechnisches Journal*, 1847, cvi, 128.



alas! prematurely, in the midst of his career so full of discoveries and of useful works. As is well known, he obtained by distilling shales from the environs of Autun: I, volatile ethereal oils, II, fixed oils, III, oils combined with paraffine from which he prepared grease for carriages, IV, paraffine suitable for making candles, &c. Among all these bodies, Mallet continues, we have only to occupy ourselves with the volatile oils. Further on M. remarks that the acid and alkaline treatment used by Selligie is similar to that proposed by Barral for products from coal-tar. Thus far, says Mallet, these hydro-carbons have found no application,\* partly on account of their insupportable odor when not purified and partly on account of their high price—about \$10.00 the hundred lbs.—when purified.

We have been at no pains to ascertain whether the industrial distillation of shales, so well grounded by Selligie, has been continued in France without interruption up to the present time, for we know of no reason to doubt the fact. Certain it is that coal-oils produced by French manufactories were exhibited, at the Exposition Universelle at Paris in 1855, and likewise in 1851 at London.†

To any one familiar with the extreme slowness with which the practical applications of chemistry are even now imparted to, and recorded by, scientific writers, it would have been no matter of surprise if the results obtained by Selligie had remained uncopied upon the records of the French patent office. Such however was not the case. From the preceding citations it will be seen that his results were published in various well known journals and were widely diffused. Dumas, in his *Traité de Chimie Appliquée aux Arts*,‡ expressly calls attention to them. They are also noticed in the *Handwörterbuch der reinen und angewandten Chemie*, von Liebig, Poggendorff u. Wöhler, 1844, iii. 364. What we cannot explain is the apparent ignorance of these facts which was exhibited by several of the leading chemists of Great Britain on the occasion, of a trial,§ Young, v. White and others held in June, 1854, in the Court of Queen's Bench before Lord Chief Justice Campbell.

Several patents for the production of oils [coal-oils] from bituminous substances were meanwhile obtained in England. Butler,|| for example, in describing his "improvements in the manufacture of oil and gas" proposes to distil bituminous shales, &c. for the purpose of obtaining oil and gas free from naphthaline. The shale, best after wetting it with water if the principal object is to obtain oil, is distilled in common gas retorts under which a gentle fire is lighted. As soon as oil begins to flow over freely the fire is to be increased and the retorts brought to a red heat; a large quantity of gas is thus obtained which is collected in a gas holder. The rough oils, as Butler informs us, may be purified by washing with sulphuric acid, filtration, &c., or they may be used in the rough state for making oil-gas. The oils in their rough state are often found entirely free from oxygen, and if obtained by the process described never contain so much as is contained in the coal-tar obtained in the coal-gas works where the coal is thrown into retorts already brought to a red heat. These oils in their rough state are further distinguished from coal-tar by their containing no naphthaline. Moreover the less volatile part of the

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\* It will be observed by the reader of Mallet's treatise that he is interested only in a single branch of the subject, viz., the volatile naphthas—"light stuffs," just as we are here giving prominence to another portion of it, viz., the fixed, or paraffine-oil; and that he holds the naphthas from shale in small repute, since in his opinion they can never compete in the matter of cost with those from coal-tar.

† A. U. MOREAN (No. 1361, Cat. 9), *Bas-Rhin*.

‡ Paris, 1844, t. vii, p. 390; also t. iii, p. 315 of the Liege edition; and B. vii, S. 510 of the German translation.

§ Reported in Barlow's London Journal of Gas Lighting, Aug. 10, 1854, vol. iii, p. 508.

|| Patent granted Jan. 29, 1833. Specification No. 6375 of the English Patent Office.

oil [No. 2] offers another characteristic feature; if after being drawn off and distilled, and if in this latter process the more volatile or first proceeds, say one half of the quantity acted upon, be set apart and the remaining half exposed to a low temperature, there will soon appear in this part of the distilled oil small flakes of a white, odorless, and light substance which is a compound of carbon and hydrogen [paraffine]. The familiarity with the subject, somewhat remarkable in view of the early date of his patent, which Butler exhibits cannot fail to strike the reader. This inventor was however unfortunate in the idea of trying to make at the same time oil and gas—in endeavoring to reconcile two antagonistic processes.

In 1841, Sept. 4, Count de Hompesch of Prussia\* specified certain “improvements in obtaining oils and other products from bituminous matters.”† It is well known, he says, that oils may be obtained from these substances but from the imperfection of the processes now used the quantity obtained is small, the quality inferior, and the smell noxious. My invention consists in an improved process, whereby I increase the quantity, improve the quality, and remove or greatly modify the smell. I have found by experiment, he continues, that the oil from shale, &c., possesses three different characters which may be called essential oil, intermediary fat oil, and thick oil, and these oils I separate by means of peculiar apparatus—which he describes in detail. In distilling shales heat is applied until the temperature reaches  $100^{\circ}$  R. =  $257^{\circ}$  F., at which temperature essential oil will pass over. The charge, after having been subjected to this temperature for half an hour, is pushed forward in the retort which is now subjected to a heat of  $200^{\circ}$  R. =  $482^{\circ}$  F., by which increased heat the intermediary or fat oil is obtained. After having subjected the charge to this increased temperature for half an hour the workmen again pushes the charge further on in the retort where it becomes of a red heat; the vapor now given off yields the thick oil. The carbonization is now complete; and I obtain these three separate oils by the gradual increase of the heat; and I effect this distillation without decomposition of the substance, the vapors escaping from the retort as fast as they are formed.

The essential oil is separated from the fat oil by exposing the mixture to a current of steam by which the more volatile oil is carried off. The oil [fixed] thus prepared must be filtered and is then ready for application to all kinds of machinery, being very fat, works without friction and leaves no sediment. The essential oil is collected and subjected to further treatment.

The specification of Du Buisson‡ for improvement in the distillation of bituminous substances, is an almost literal translation of Selligie’s last patent. Indeed, Du Buisson tells us that the extensive works at Autun, Department of the Saone and Loire, France, are partly his property and that he has the management of them as chemist. He affirms moreover that the most important results have there been attained—results which place the distillation and treatment of schistus among the most useful and productive of chemical manufactures.

Since we have already extracted largely from Selligie’s specification it is unnecessary to cite more of it here. It is a little curious that this most important patent is not mentioned in Dr. Antisell’s “list of English Patents” (p. 141).

The well known attempts to prepare paraffine and oils from peat§ need not be discussed here. Another patent, not mentioned in Dr. A.’s list, is that of

\* Specification No. 9060 of the English Patent Office.

† In a “memorandum of alteration,” dated July 5, 1842, de Hompesch claims the right of distilling “bituminous schists, shales, or slates, or other rocks or minerals containing bitumen or bituminous substances.”

‡ Dated June 23, 1845. Specification No. 10,726 of the English Patent Office.

§ Antisell, p. 85; compare Rees Reece’s patent dated Jan. 23, 1849. Specification 12,436 of the English Patent Office.

George Michiels.\* It is peculiarly interesting since a portion of it relates to the preparation of oils from caking coals. Michiels proposes in fact to prepare coke from bituminous coals, and from mixtures of such coals with anthracite, by moistening the powdered coal with water and introducing it—in charges of six tons—into brick retorts furnished with ordinary condensing apparatus and other appliances. The retorts are then heated as if it were intended to produce gas, with this difference, that the temperature for the first fifty hours should not exceed nascent red heat, or  $964^{\circ}\text{F.}$ ; after that time it should be increased progressively until it attains a clear red heat, which would be about the ninety-sixth hour. I should remark, continues Michiels, that about the sixtieth hour I shut off the communication between the retort and the condensor by closing the hydraulic valves, and at the same time open the valve on top of the retort, &c., so as to allow the air to enter, which burns the hydrocarburets [now being evolved] and the products of that combustion heat the retort, &c. in passing through the flues which surround the retort. \* \* \* I thus obtain coke, ammoniacal liquors and liquid hydro-carburets. These “hydro-carburets” were repeatedly distilled by M. in order to obtain as much light volatile oil as possible, A heavy yellow oil of density 0.911, or lower, was also obtained which according to M. will be found applicable to many useful purposes, and is suitable for his principle object of turning into gas.

Further on (p. 15 of his specification) Michiels explains that this oil is well adapted for manufacturing gas upon a small scale, since the gas prepared from it requires no purification, and since it can be used in any of the ordinary apparatus for making gas from camphene, oil, or resin. In a word, he proposed using it just as rosin oil is now so largely employed by private gas-works in this country, or as Boscary and Butler had used the same coal-oil before him.

We pass† to a consideration of the well known labors of Mr. James Young of Glasgow.‡ From evidence brought forward in the trial already cited it appears that Mr. Young's attention was called in 1847 to a mineral oil [petroleum] found exuding from a coal pit at Riddings in Derbyshire. From it he obtained a good lubricating oil which he continued to prepare as long as his supply of petroleum lasted. Occupied as he was with the subject it can surprise no one that he should soon have turned his attention to the distillation of the highly bituminous mineral of Torbane-hill, now known as Boghead coal in England and in this country, which was introduced to public notice in 1850.§ From this substance Young was enabled to prepare a much larger amount of oil per ton of mineral than had been obtained by any of his predecessors. To the discovery of the vast source of an admirable raw material which the Boghead mine furnished is evidently due the immense increase in the production, and of course consumption, of coal-oil which immediately ensued. To this we say, more than to anything else is to be attributed the rise and progress, during the past few years, of the almost innumerable manufactories of coal-oil on the continent of Europe and in our own country. From the impetus thus given, a branch of industry which had long been, comparatively speaking, of only local importance soon attained an enormous development.||

\* Granted April 30, 1850. Specification No. 13,066 of the English Patent Office.

† Making no pretence, be it understood, that we have been able to collect all that has been published upon the subject before 1850.

‡ Patent dated Oct. 7, 1850.

§ According to Mr. T. G. Barlow, *London Journal of Gas Lighting*, iii, 519.

|| We cannot, in this connection, forbear quoting the following pertinent remarks from Lord Campbell's charge to the jury in the case—*Young v. White* and others (see *London Journal of Gas Lighting*, iii, 521)—already cited.

“And this brings me to an observation,” says his Lordship, “which I meant to make, and which I should have been sorry if I had forgotten, which is this—that it was the discovery of this Boghead coal that seems to have given the great value



Let it be distinctly understood that we would in no wise detract from the real merit of Mr. Young. Uniting, as he does, no small share of chemical knowledge with the cautious, untiring energy of his countrymen, few men could have been found better qualified to grasp the golden opportunity of which he so fortunately availed himself. His name must ever remain associated with those of the distinguished observers from whose labors this most important branch of industry has resulted. It is Dr. Antisell only whom we blame for his incorrect and partial "history." When, for example (on p. 14), Dr. A. tells us that: "only since the year 1850 has the manufacture of paraffine from pit-coal, turf and bituminous shales succeeded as an art. The first manufacture was that of James Young in Manchester, by whose process, from 100 parts of Cannel-coal 40 per cent of oil and 10 per cent of paraffine could be obtained." He makes a statement which is grossly exaggerated—if not *entirely* at variance with fact—as our readers must already have perceived.

We willingly quote what follows: "In thus showing [*i. e.*, dogmatically *asserting*] that the practical manufacture of oils from coal is due to James Young, it may not be amiss to call attention to what it was which he produced from coals by distillation. He claimed the production of paraffine oils—not the production of naphtha or benzole [benzol?], nor naphthalin, but paraffine and its congeners: this involves the slower distillation of coals at a lower temperature than had been hitherto effected, and this novelty in practice was followed by the novel result of a copious production of isomeric liquid hydrocarbons; so that really two great results were first demonstrated, practically by the operation of Young's process, namely—1st, That coal was a material from which liquids could be manufactured economically, as tar, bitumens, and schists had been hitherto employed; and 2nd, That the liquids so formed were paraffine-containing compounds." Having merely to suggest that the sentence might have been more tersely put. For in truth it means only—if it means anything—that in the opinion of Dr. A., Mr. Young was the first person who distilled coal [on a manufacturing scale?] at comparatively low temperatures. What Dr. Antisell's private views regarding "low temperature" or "practical" may be, we are ignorant. But we do know that when, 30 years ago, Reichenbach distilled quantities of coal of 75 lbs. weight each, and exercised the greatest care in maintaining the temperature of his retort at as low a degree as was admissible, as he has most minutely described in the memoirs which we have already cited;—when he obtained paraffine and eupion as results of his operation; he most certainly demonstrated the practicability and the manner of preparing both paraffine and "paraffine-oil."

All this however does not appear to satisfy Dr. A. in the least degree, who repeatedly assures his readers that the manufacture of oil from *coal* dates from the patent of Mr. Young. Since our author has seen fit to dwell at length upon this point and to devote so much space to its discussion we may be pardoned for referring to it here.

As is well known the term "coal" is applied in common language to a great variety of mineral combustibles no two kinds of which are precisely alike while some sorts are exceedingly unlike others. The term is at best merely conventional; used, in lack of any better one, to designate substances with the real nature of which we are still almost entirely ignorant.

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to paraffine, because until then I do not find it was obtained in such quantities as really were of any considerable value; but the Boghead coal now being discovered, and this schist or coal being discovered, which is of very rich quality, and having a great deal of what is the essential part of the paraffine; from that time it has become much more important; and that may explain why, although the mode of obtaining paraffine was before well known, it should not have been put in practice because it would not appear that it could be put into practice with much profit or benefit, unless you had such a substance as Boghead coal on which you could operate."

In confirmation of this view compare also: Payen, *Précis de Chimie Industrielle*, 4e Ed. Paris, Hâchette. 1859. t. ii, p. 685.

With the flint-like anthracite of Wales, the beautiful Albert coal\*—but a step removed from asphaltum—of Hillsboro, New Brunswick; our common lignites, frequently shading into peat, and the bituminous shales as frequently passing by insensible gradations into common slate, as points upon its extreme limit, we have within the circumference of the circle an infinite number of substances, shading into each other by scarcely perceptible degrees,—all of which are, in technological language at least, varieties of *coal*. The “amplitude of variation” which this species, or rather this term, enjoys is indeed so great that it would be a matter of no small difficulty to choose any single member of the medley as a central point, or even to conceive of an ideal coal to which all other varieties should be referred. In attempting any such selection a native of one of our sea-board states would assuredly lean towards anthracite; the South-German towards his excellent lignites; the Scotchman towards his cannel; while Newcastle would claim a proverbial right of precedent. We would, for our own part, vote for the last named, or some other good caking coal, capable of furnishing both gas and serviceable coke, and of being used for an infinite variety of purposes. Starting from this then as a type, observe, that as we pass towards the cannels, the different varieties of coal become better and better suited for the manufacture of gas or oil, *i. e.*, they contain more and more hydrogenous compounds. The appearance of the mineral meanwhile approaching more and more closely to that of slate, while at the same time the value of the fixed carbonaceous residue becomes less and less, soon ceasing to be “coke” at all, but rather a more or less carbonaceous slate. At length a maximum of hydrogenous matter is reached as in the case of Boghead coal, a slaty substance, the fixed residue from the distillation of which is a slightly carbonaceous stone, valueless as fuel and useful only, as a substitute for bone-black, for purposes of disinfection or decolorizing liquids, uses to which the residues of the French shales have long been applied. Beyond this maximum, as the amount of gas and oil-producing substances diminishes, and the amount of earthy matter increases,—taking the place of the fixed carbon in our typical caking coal, we pass into “bituminous shales,” and these become less and less bituminous until at length we reach common clay slate containing no organic matter whatsoever. We have here traced no fancy sketch. That the “cannel coals” thus gradually pass into “bituminous shales” is now well enough known, at least to gas engineers and other practical observers. It would not for that matter be exceedingly difficult to obtain a continuous series of specimens exhibiting this almost insensible gradation. Now did Mr. Young devote his attention to the distillation of caking coals similar to our typical Newcastle? By no means! On the contrary we find him occupied with a mineral which was called indifferently “shale” or “coal,” until it was in 1853 decided in a Scottish court that it should henceforth be legally known as coal.†

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\* On page 18 of Dr. A.'s work the following remark occurs. “In one respect they [bitumens] differ from coal. In no case can an organic tissue or structure be demonstrated when they are examined under the microscope. Viewed in this light the mineral found at the Albert mine, New Brunswick, should be classed as a bitumen since Dr. J. Leidy was unable to detect any trace of structure in its mass.” We cannot understand the motive of our author in thus again dragging to light this negative result, for it is perfectly well known to the scientific men of America that Prof. J. Bacon detected the existence of vegetable structure in the interior of masses of the Hillsboro coal. See *Reports on the Geological Relations, chemical analyses, and microscopic examination of the coal of the Albert Coal Mining Co., situated in Hillsboro, Albert Co., N. B.*, by Chas. T. Jackson. M.D. New York: printed by Nesbitt, 1851, p. 30; compare this Journal, [2], xiii, 276.

† We had supposed, when the above was written, that the decision of this court had been sustained. That in this we were mistaken appears from the following, which we extract from a statement in a late number of the *London Journal of Gas*



We would cast no reflection upon the judgment rendered in this famous suit. Looking at it as a mere matter of equity, depending upon the business relations of the parties at issue, this verdict was in our own opinion, just. But the fact of this mineral being, or not being, called a *coal*, does not in the least degree prevent it from being *also a shale*; and that it is more nearly related to the shales than to the coals is believed by a large proportion of those who are intimately acquainted with it, be they scientific or practical men. We have no space to discuss at greater length this quibble of Dr. Antisell's—which, however excusable it might have been in a retained attorney or solicitor of patents, is anything but becoming to the chemical professor or the historian—being content to refer the reader to the published reports of the trial just mentioned. We will here cite only a few lines\* descriptive of Selligie's mineral: "The quantity of oily matter in these shales is very variable and often very

*Lighting* (Jan. 17th, 1860. vol. ix, p. 41), received as this article is going through the press.

"SETTLEMENT OF THE GREAT TORBANE-HILL CASE.

We have been favored with the following particulars connected with the well known case, the 'Bathgate or Boghead Gas Coal *alias* the Torbane-hill Mineral,' which has lasted upwards of seven years, having passed through several phases in the Supreme Law Courts of Scotland and England. A compromise was finally come to on Wednesday last, the eleventh current. It is embodied in a minute of agreement between Mr. and Mrs. Gillespie of Torbane-hill, of the first part, and Messrs. James Russel and Son, and James Russel, Esq., of Blackbraes, of the second part.

The preamble of the minute of agreement, which itself consists of twelve articles, is as follows:

'The said parties, considering that disputes and differences have arisen between them and a lengthened litigation has taken place, with respect to the missives of agreement for a lease of certain minerals in the lands of Torbane-hill, entered into betwixt the said first party hereto on the one part, and the said company of James Russel and Son, and individual partners thereof, on the other part, and dated the 30th of March and 1st of April, 1850; and both parties being now desirous that the said litigation should be brought to an end, and all disputes and differences between them amicably adjusted and settled, they have agreed, and hereby mutually agree and bind themselves as follows:—

The first two articles provide that the actions at present depending shall be abandoned, as a consequence of the execution of the minute.

The third article provides that each party pay their own expenses.

The fourth article, which has for title 'Name of Mineral,' is both an important and curious one—important in a scientific point of view, and curious as illustrative of the pertinacity with which either party have clung to their own views. The article is as follows:—'Whereas the second party have been, and are, working in the said lands of Torbane-hill, and disposing of, under the name of Bathgate or Boghead gas, parrot, or cannel coal, a mineral which they, the second party, deemed and deem to be a parrot or cannel coal, and which the first party deemed and deem to be a new mineral substance, having an argillaceous base, and to be of so peculiar a nature as to constitute it in truth a new and very peculiar variety of bituminous schist, slate, or clay, and have been for some time in use to call 'the Torbane-hill Mineral'; it is hereby agreed that, throughout the remainder of these presents, where the mineral in question is named, it shall be called for the sake of brevity the disputed mineral.'

Article fifth relates to the subject of a portion of Torbane-hill which was reserved from the operation of the mineral lease, and by this article 'the disputed mineral,' as we now call it, contained in the reserved portion of the estate, may be worked or let by the proprietors, without the danger of any obstruction being offered by the second party in the agreement." \* \* \*

\* From Dufrénoy et Elie de Beaumont's *Explication de la Carte Géologique de la France*. Paris, Imp. Royale, 1841. t. i, p. 673.



considerable. According to M. Xardel some rare samples exist which afford even 45 @ 50 per cent; \* \* \* other specimens afford 20 @ 25 per cent. The beds which are worked, or are capable of being worked, yield from 5 to 9 per cent." [p. 675].—Again [p. 676], "The impressions of fossils, so common in the shales of d'Igornay, occur in the poorer shales. The rich shales, on the contrary, often contain vegetable remains analagous to those commonly found in the coal measures. Perhaps the beds of rich shale are in a manner the representatives of coal-beds; it is to be remarked that in the shale which yields 9 per cent of oil its sheets are covered with a multitude of shining (*miroirantes*), lenticular veins, having a waxy fracture, which by their aspect and manner of burning recall the variety of coal which is called *cannel coal*."—Leaving it for our readers to answer the question; how far removed in anything but productiveness is the "coal" (Boghead) upon which Mr. Young has operated from the "*shale*" distilled by M. Selligie?

It may not be amiss to mention the fact that upon the continent of Europe the Boghead mineral is almost universally called, not coal, but shale. A fact with which the reader can readily enough familiarize himself by consulting the German chemical journals of the last eight or ten years. In proof of it we cite only the following: \* "The recent verdict in the celebrated Torbane-hill-mineral case appears to be contrary to the scientific opinions held in Germany, as proof of which we have a case in point, and which, although not at the time known in this country, was officially decided upon in Berlin previous to the trial coming on in Scotland, which terminated on the 4th of August last. It appears that in Frankfort-on-the-Main there has, for some time past, been in existence a company for lighting the streets and houses by gas from oil, resin, &c. A rival English company contracted to light with coal-gas; and to give both fair play, it was decided that the latter company should be confined to the use of coal alone. Mr. Engelhard, the manager of the Oil (Resin) Gas Company, having heard of the Boghead and Torbane mineral, obtained specimens, and having found they produced excellent gas, gave an order for a large consignment which reached Frankfort *viâ* Rotterdam, through a Dutch agent. This was entered at the Custom-house as *cannel coal*, much to the annoyance of Mr. Engelhard, who was no more at liberty to make gas from coal than his rivals were to make it of anything else but coal. He was, however, prevented from the necessity of a trial at law, for the officials did not feel themselves justified in charging the duty as coal, although, as other mineral, it would pass free, and applied to higher authorities for instruction. These parties were as much at a loss as their inferiors, and the case was eventually transferred to the Central Board of Customs at Berlin, the last court of appeal of the Prussian *Zollverein*, where all disputed questions in the German States are settled. Scientific men, connected with the board, examined the Boghead and Torbane mineral and decided that it was not coal, but *bituminous shale*, which is said to be the general opinion among German chemists. It has been admitted into Germany, duty free, and Frankfort is now partially lighted with gas from this mineral, charged for as resin or oil gas. It is described as a clay containing bitumen, and producing oil when heated. At all events, we may take this German decision as impartial as, had it been admitted as *cannel coal* it would have been subject to a duty varying from 1s. to 1s. 6d. per ton."

In connection with the question of the products of the distillation of *coal* which Dr. A. would have us believe so entirely new to the world and to this country in particular, we cite the following from The *Encyclopædia of Chemistry*, by James C. Booth and Campbell Morfit. 8vo, Philadelphia, Baird, 1850, p. 461. Article, Coal: paragraph, "products of dry distillation."

\* See *London Journal of Gas Lighting*, Oct., 1853, iii, 256; from *London Mining Journal*.

"These products [of the dry distillation of coal] are somewhat analogous to those derived from wood, and some are identical with them. \* \* \* The liquid products consist of various bodies closely allied to petroleum, and the solids *Naphthaline* and *Paraffine*. The relative proportions of these products vary with the temperature. The lower the heat employed, the less gas, and the more solids and liquids are produced; the higher the temperature the greater is the quantity of carburetted hydrogen." Before closing this sketch we must refer to and correct a palpable error of Reichenbach's\* which has been cited by Dr. Antisell (p. 14), from whom we quote it: "So remained paraffine until this hour [date of Y.'s patent], a beautiful item in the collection of chemical preparations; but it has never escaped from the rooms of the scientific man."

Upon the reader who has followed us thus far we need not urge that the above statement is incorrect. As an offset to it we cite the following:†

"In the Parisian Industrial Exhibition for 1839 Selligie exhibited: 1st.—Bituminous shale, then fluid bitumen [crude oil], mineral grease, crude and refined (the former at 50 fr. the 100 kilog. [= \$5.00 per 100 lbs.]), also *mineral wax* [paraffine] crude and refined (the former at 125 fr., the latter at 180 fr. [= respectively 12½ and 18 dollars per 100 lbs.]). The purified mineral wax was beautifully white but the candles made of it had a soiled appearance." V. Hermann (now, according to Wagner, councillor of State in Munich goes) on to assert that "if these fatty products can be prepared economically they belong to the most important objects of the Exhibition."

It would be foreign to our purpose were we to attempt to trace the recent history of the art of manufacturing coal-oil, even if our space allowed of it. During the past few years a large number of papers‡ on the subject have been published in the Scientific Journals of Germany; while several recent works upon the materials used for producing light have each devoted a separate chapter to its description. A few special treatises have also been published of which the following is a, doubtless very incomplete, list.—§

UHLENHUTH, Ed. *Handbuch der Photogen- und Paraffin-Fabrikation aus Torf, Braunkohle und bituminösem Schiefer nach den neuesten Versuchen und Erfahrungen.* Quedlinburg, Basse, 1858.

MUELLER, Carl, Georg, *Die trockene Destillation und die hauptsächlichsten auf ihr beruhenden Industriezweige.* Leipzig, Barth, 1858.

DANCKWORT, MEITZENDORFF and WERNECKE. [Committee of the Magdeburg Gewerbeverein.] *Ueber das Photogen oder Mineralöl, so wie die ihm*

\* Erdmann's Journal für praktische Chemie, lxiii, 63. Did our space allow, we would gladly transcribe the whole of this article—an English translation of which may be found in the London, Edinburgh and Dublin Philosophical Magazine, [4.] viii, 463—in proof of our assertion that the present widely-spread manufacture of coal-oil and paraffine is mainly due to the comparatively recent discovery of rich stores of highly bituminous substances.

† From v. Hermann's *Die Industrie Ausstellung zu Paris im Jahre, 1839, Nürnberg*, 1840. p. 147;—in Wagner's *Jahresbericht ueber die Fortschritte der chemischen Technologie*, 1855, i. 416.

‡ Very complete synopses of these may be found in Wagner's *Jahresbericht*, four volumes of which have thus far been published. For references to the recent admirable *scientific* researches of GREVILLE WILLIAMS, DE LA RUE, and others, which have been chiefly confined however to the more volatile portions of the oil and to the basic compounds which occur in it, see Liebig and Kopp's *Jahresbericht der Chemie*, u. s. w.

§ Small as this list is, it will nevertheless recall to the mind of the reader the modest lines with which Dr. Antisell's preface commences, namely these: "the present little treatise is the first published monograph on the art of distilling oils from minerals containing Bitumen."

## 20 Review of Dr. Antisell's Work on Photogenic-Oils, &c.

*ähnlichen Leuchtstoffe, in Bezug auf ihre Feuergefährlichkeit und ihre Anwendung.* Magdeburg, 1856.

Also the insignificant brochure of SCHRADER, F. W. *Ueber die industrielle und national-ökonomische Bedeutsamkeit der Gewinnung von Chemikalien insbesondere des Paraffin's und Photogen's aus dem Kohlentheer, u. s. w.* Ascherleben, Beyer, 1856.

This article must here close. Leaving unnoticed several inaccuracies which we had intended to discuss we will dismiss the subject with two brief quotations. The first from Dr. Antisell's book, p. 15. "An impression has taken hold of the American manufacturing public that the patent of James Young has no force, as it was not a new invention at the date of the patent; and from the unfavorable effect of that patent upon the actual manufacture of coal-oils in this country, an ill-feeling has been produced against it. That the owners of this patent have not acted wisely by withholding sales and licenses under it until very lately, is to be regretted; but that it was a *bona fide* improvement in an art at the time when it was patented, and that therefore the patent was rightly issued in this country, there can be no shadow of a doubt in the mind of any one who carefully traces the steps of the discovery of the production of photogenic oils from different materials."

The second from Lord Chief Justice Campbell's charge\* to the jury in the case already alluded to. "Now gentlemen I direct you, in point of law, that if there were books then [at date of Young's patent, 1850] in circulation in England disclosing this mode of obtaining paraffine and paraffine oil which were known, were accessible, that the patent would be invalid, although Mr. Young never read those books, and although that mode had not been actually put in practice. If there were books in England in circulation, accessible to all who were interested in the subject, which disclosed this, and would instruct them and enable them to obtain the paraffine and the paraffine oil from the distillation of bituminous substances, then Mr. Young's patent would be invalid."

FRANK H. STORER.

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\* *Loc. cit.*, p. 520.



## NOTE ON SOURCES OF ERROR IN THE EMPLOYMENT OF PICRIC ACID TO DETECT THE PRESENCE OF POTASH.

By M. CAREY LEA, PHILADELPHIA.

[Read before the Am. Assoc. for the Adv. of Sci., at Newport, August, 1860.]

PICRIC acid enjoys a high reputation as a test for potash. Employed in its alcoholic solution, or as soda or ammonia salt sometimes as magnesia salt, it gives with potash solutions a dense yellow crystalline precipitate. If the solution containing potash be very dilute, the precipitate may not make its appearance till after some hours repose, and it then forms long delicate needles.

Rose remarks that this reagent "is even more sensitive than the solution of chlorid of platinum." In his summing up, he observes, that of the various reagents, chlorid of platinum, tartaric acid, picric acid, perchloric acid, sulphate of alumina and hydrofluosilicic acid, the latter is insufficient to distinguish between potash and soda; and that the chlorid of platinum and sulphate of alumina give the same reactions with ammonia as with potash.\* No qualification is made with respect to the certainty of the indications afforded by picric acid. Plattner makes the same observation as to the greater sensitiveness of picric acid compared with bichlorid of platinum and equally without qualification as to its reliability.†

I therefore believe that the remarkable insolubility of otherwise soluble alkaline picrates, in alkaline solutions has not been before pointed out. If an alcoholic solution of picric acid be poured into a solution of carbonate of soda, it occasions an immediate dense yellow precipitate, not to be distinguished in appearance from a precipitate of picrate of potash, and liable to be mistaken for it with the greatest facility. The picrate of soda formed in the case just mentioned is the most soluble of all the alkaline picrates, and *a priori* we should not expect to find it precipitated under these circumstances: an aqueous solution of picrate of soda added to one of carbonate of soda acts in precisely the same manner.

To ascertain if these reactions were extended to various compounds of picric acid, examinations were made which gave with the following results:

Alcoholic solution of picric acid added to—

solution of carbonate of ammonia, gave an immediate dense yellow crystalline precipitate.

" carbonate of soda gave not so instantaneous a precipitate, but one which after standing became even more dense.

\* Rose, Handbuch der Analytischen Chemie, 1<sup>r</sup> Band, 6-10 S.

† Plattner, die Probirkunst mit dem Lothrohre, 3d Ed. p. 178.

Aqueous solutions of picrate of soda gave with  
 solution of carbonate ammonia, }  
 sulphate of ammonia, } abundant precipitates.  
 carbonate of soda, }  
 phosphate of soda, } slight precipitate.

Aqueous solution of picrate of ammonia gave with  
 solution of carbonate of ammonia, }  
 " sulphate of ammonia, } abundant precipitates.  
 " carbonate of soda, }  
 " phosphate of soda, } none.

Aqueous solution of picrate of magnesia gave with  
 solution of carbonate of soda, }  
 " carbonate of ammonia, } abundant precipitates.

When the alkaline solutions to be tested are otherwise than very dilute there is absolutely no difference in the appearance of the precipitates. When the amount of precipitate is small, the following differences may be observed:

The potash precipitate forms longer needles, and when these are found only after standing, or when the precipitate is redissolved by heat and allowed to crystallize by slow cooling, they exhibit a beautiful play of red and green colors.

The soda salt is of a lighter and brighter yellow than either the potash or ammonia salt. Its needles are also shorter than those of either of the other compounds, and when the precipitate has been redissolved by heat, and allowed to crystallize by slow cooling, they tend to agglomerate themselves together in spherical masses. This is a very marked character, and when exhibited, is unmistakable, but is not always shown.

The ammonia salt when crystallized in quantities is very distinct in appearance from the potash salt, but when thrown down in small portions, even by slow crystallization, cannot be distinguished from it with certainty. The prisms are flatter, but these differences are not apparent in very slender needles. The play of colors which the ammonia salt exhibits to a less degree than the potash, disappears entirely in the soda salt.

The above reactions indicate that extreme caution must be used in employing picric acid as a test for potash. The precipitates above described do not redissolve in any excess of the picrate, or of picric acid; nor is it to be supposed that concentrated alkaline solutions are necessary to cause them—on the contrary, in many cases, very dilute ones are sufficient. To determine within what limits such reactions are produced, the following trials were made:

A. Dilution of the alkaline solutions. Limits obtained,  
 (I.) With carbonate of soda,

A solution containing 5 per cent anhydrous carbonate of soda gave with alcoholic solution of picric acid, an immediate abundant precipitate, in 10 minutes the tube could be inverted without spilling the contents.

with solution picrate of soda, an immediate precipitate becoming in the course of an hour a very dense one.

A solution containing  $2\frac{1}{2}$  per cent carbonate of soda gave with alcoholic picric acid, a slight precipitate increasing very much by standing, so that after 18 hours the tube could be inverted without spilling the contents.

with picrate of soda, none.

A solution containing 1 per cent carbonate of soda gave with alcoholic picric acid, slight precip. after 18 hours repose.

with picrate of soda, none.

(II.) With sulphate of ammonia,

A solution containing 5 per cent anhydrous sulphate ammonia gave with alc. picric acid, immediate dense precip.

" picrate soda " " "

solution containing  $2\frac{1}{2}$  p. c. sulph. ammonia gave with alc. picric acid, immediate dense precip.

solution containing 1 p. c. sulph. ammonia gave with alc. picric acid, immediate dense precip.

" solution picrate soda, immediate slight precipitate. The solution on standing gave a beautiful crystallization of long needles with bright play of colors, exactly resembling the reaction of potash salts.

" picrate magnesia, by long standing, a very faint precip.

" picrate ammonia, none.

solution containing  $\frac{1}{250}$  anh. sulphate ammonia gave with alc. picric acid, after a short interval an abundant precipitate.

solution containing  $\frac{1}{500}$  anh. sulph. ammonia gave with alc. picric acid, after a short interval, a considerable precip.

solution containing  $\frac{1}{1000}$  anh. sulph. ammonia gave with alc. picric acid, no precipitate, even after twenty-four hours' repose.

B. Limits obtained with respect to indications of diluted solutions of alkaline picrate.

A solution of picrate of ammonia in 200 parts water gave—with an equal volume of strong solution of carbonate of ammonia, an immediate precipitate of small yellow needles—in 10 minutes a considerable quantity settled at the bottom of the vessel.

A solution of same salt in 400 water gave with an equal volume of solution carbonate ammonia, signs of a precipitate in a few minutes, and after some hours an appreciable quantity settled at the bottom of the vessel.

With 1 part picrate ammonia in 800 water no precip. was produced by solution of carb. ammonia even after 24 hours' repose.

The conclusion to be drawn from these results is,

That alcoholic solution of picric acid or aqueous solution of picrate of soda will produce a precipitate in almost any alkaline solution, whether of soda, ammonia or potash, except under cir-



cumstances of great dilution, especially if allowed to repose for 24 hours.

That picrate of ammonia and picrate of magnesia give the same results, but in a less degree.

That picric acid is therefore wholly unreliable as a test for potash; the results obtained being such as would tend altogether to mislead those who are not extremely familiar with the appearance of the precipitates, and that in some cases the results are so deceptive that even eyes most familiar with these reactions might be deceived; for example, in the result obtained above by testing a solution containing 1 per cent. sulphate of ammonia with solution of picrate of soda. In this case a crystallization of picrate of ammonia was obtained perfectly simulating that of the potash salt.

Picric acid is in fact a better test for soda, than for potash, because with a soda solution it gives a precipitate which redissolved by heat generally (but not always) gives a characteristic spherically radiated, bright canary yellow crystallization, whereas the precipitate obtained from a potash solution can never be positively distinguished by its appearance from that afforded by an ammonia solution, and we have just seen that a solution containing  $\frac{1}{2} \frac{1}{10}$  of sulphate of ammonia or even less, is capable of producing such a precipitate.

Philadelphia, Feb. 23d, 1860.

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## ON A SERIES OF NEW COMBINATIONS OF AMMONIA, PICRIC ACID AND METALLIC BASES.

By M. CAREY LEA.

[Read before the Am. Assoc. for the Advancement of Sci., at Newport, Aug. 1860.]

IN a paper published in this Journal, vol. xxvi, 379, for 1858, I described two compounds of picric acid and ammonia with copper and nickel respectively, and mentioned their instability and the great difficulty of obtaining them in a state of tolerable purity. Since then I have found that many other metals form compounds of a similar nature, and have succeeded in obtaining several of them sufficiently pure for approximate analysis. The results obtained are given below—other investigations are in progress and I hope to communicate them hereafter.

When a metallic salt is precipitated by ammonia, and a large excess of the precipitant added, a more or less complete solution of the precipitate is frequently obtained, especially if a considerable quantity of ammoniacal salt be present. I have found that these ammoniacal solutions when treated with an alkaline picrate, for the most part yield an immediate precipitate containing

the elements of a metallic picrate united with those of ammonia. These precipitates are often very beautiful, they are generally yellow or yellowish, somewhat soluble in the mother liquid, or in strong ammoniacal solutions by aid of heat, nearly insoluble in water and decomposed by it very readily, especially if it be present in quantity, or heat be applied. Thrown on a filter and washed, the picric acid, ammonia, and some portion of undecomposed salt in solution pass through, while the greater part of the metallic oxyd remains on the filter and with sufficient washing is perfectly freed from picric acid and ammonia, and presents the appearance of a pure hydrate.

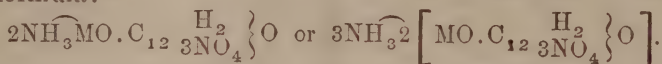
The analyses of these substances were made in the following manner. It was found desirable that before the ammonia and metallic oxyd were determined, the whole of the picric acid should first be removed. This was effected by adding chlorhydric acid to a weighed quantity of the substance carefully dried, and evaporating to dryness at a gentle heat. Ether, which must be anhydrous or nearly so, was added in the proportion of 15 to 18 grammes to .6 or .7 gms. of the salt used, detaching the dry crust and breaking it up to powder with a glass rod that every part might be brought thoroughly in contact with the ether. After standing ten minutes the ether was poured off, a fresh quantity added, and a larger beaker was inverted over that which contained the substance undergoing analysis. After a lapse of three or four hours the liquid was poured off, a third, and, if necessary, a fourth, quantity added in the same way. The decantation is effected with the greatest ease, as, if the ether is sufficiently strong, the chlorids remain nearly or quite dry at the bottom. It was found that by this means the picric acid could be separated with sufficient exactness to afford a tolerably correct estimation of its quantity, a careful trial with a weighed quantity of perfectly pure picric acid showed that the result fell a little under the truth by reason of a small loss arising from minute portions of the acid remaining undissolved. On the other hand, no chlorids are dissolved when the operation is properly performed: the ethereal solution evaporated to dryness, and the residue dissolved in water was not troubled by solution of nitrate of silver.

The operation requires nice manipulation, otherwise the loss of picric acid is considerable, and if the ether be not sufficiently anhydrous, portions of the chlorids may be removed by it.

In this manner the quantity of picric acid was determined, and from it was calculated the quantity of the group  $C_{12}H_2N_3O_{14}$ , or picric acid minus the equivalent of hydrogen which is replaceable by a metallic oxyd; in other words, the group which by union with a base forms a picrate, or by union with hydrogen forms picric acid. From the residue undissolved by the ether, the ammonia was determined either by distillation with solution of caustic soda, or by precipitation with bichlorid of platinum.

From another portion the metallic oxyd was found by appropriate means.

As far as examined, the ammonia-picrates all contain more than one equivalent of ammonia, and are represented either by the formula:—



#### *Ammonia-picrate of silver.*

Nitrate of silver dissolved in water and treated first with excess of ammonia, and the resulting clear solution mixed with cold saturated solution of picrate of ammonia gives immediately an abundant highly crystalline light yellow precipitate of ammonia-picrate of silver, which is to be thrown upon a filter, thoroughly washed with dilute ammonia, and dried in vacuo over sulphuric acid.

It is to be observed that in the formation of this, as well as of all the other salts here described, the metallic solution must invariably be in excess to check as far as possible the precipitation of picrate of ammonia together with the compound sought. I have shown in a paper intended to be read at the same time as this,\* that if an alkaline picrate be poured into an alkaline solution, a precipitate of alkaline picrate takes place. When the alkaline solution is strong the precipitate is immediate, and in the ammoniacal solutions used in the preparation of these salts any excess of alkaline picrate would fall with the ammonia-picrate. Even with every precaution, it is difficult and in some cases apparently impossible to obtain the ammonia-picrate perfectly free from this impurity.

#### *Analysis.*

|       |           |      |       |                             |
|-------|-----------|------|-------|-----------------------------|
| ·4245 | substance | gave | ·2632 | picric acid.                |
| ·5865 | "         | "    | ·3600 | " "                         |
| ·4245 | "         | "    | ·1577 | chlorid of silver.          |
| ·5865 | "         | "    | ·2177 | " "                         |
| ·3788 | "         | "    | ·4932 | chloroplatinate of ammonia. |

This leads to the formula:—



Dried over sulphuric acid in vacuo:—

| Calculated.                                      |   |   |   | Found. |       | Mean. |
|--------------------------------------------------|---|---|---|--------|-------|-------|
|                                                  |   |   |   | 1.     | 2.    |       |
| $\text{C}_{12}\text{H}_2\text{N}_3\text{O}_{14}$ | - | - | - | 61·62  | 61·73 | 61·42 |
| Ag                                               | - | - | - | 29·19  | 27·96 | 27·95 |
| $2\text{NH}_3$                                   | - | - | - | 9·19   | 9·93  | 9·93  |
| <hr/>                                            |   |   |   | <hr/>  | <hr/> | <hr/> |
| 100·00                                           |   |   |   | 99·62  |       | 99·30 |

\* See page 75.



The silver falls below, and the ammonia exceeds the calculated amount in consequence of the impossibility of obtaining the salt quite free from admixed picrate of ammonia.

This beautiful salt appears to be one of the most permanent of this very unstable class of substances. It dissolves readily in hot water containing ammonia, sparingly in cold, and crystallizes in fine needles from the hot solution. Heated on platinum foil it detonates and leaves a brilliant spot of metallic silver.

*Ammonia-picrate of copper.*

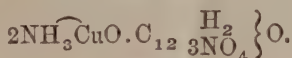
A cold saturated solution of picrate of ammonia added to an ammoniacal solution of sulphate or nitrate of copper, immediately throws down an abundant precipitate which after washing with strong solution of carbonate of ammonia and afterward with dilute ammonia exhibits a beautiful pale greenish yellow color with a shade of red through it. It is in fine scales and much resembles the dust of the wings of butterflies.

Analysis gave for this salt a constitution similar to that of the silver salt.

|        |                |      |       |                          |
|--------|----------------|------|-------|--------------------------|
| ·6059  | gms. substance | gave | ·4652 | picric acid.             |
| ·9310  | "              | "    | ·1279 | oxyd of copper.          |
| 1·4240 | "              | "    | ·1577 | metallic copper.         |
| ·6059  | "              | "    | ·2190 | chlorhydrate of ammonia. |

The copper was determined in the one case by precipitating the cupric solution while boiling with hyposulphite of soda, dissolving in aqua regia, evaporating to dryness, redissolving in dilute chlorhydric acid, and precipitating with distilled zinc and estimating as metallic copper—in the other by precipitating at 212° by caustic soda.

These results lead to the formula:—



Dried over sulphuric acid in vacuo:—

|                                                  | Calculated.  | Found. |       | Mean.       |
|--------------------------------------------------|--------------|--------|-------|-------------|
|                                                  |              | 1.     | 2.    |             |
| $\text{C}_{12}\text{H}_2\text{N}_3\text{O}_{14}$ | 77·63        | 76·44  |       | 76·44       |
| Cu                                               | 10·79        | 10·97  | 11·07 | 11·02       |
| $2\text{NH}_3$                                   | 11·58        | 11·52  |       | 11·52       |
|                                                  | <hr/> 100·00 |        |       | <hr/> 98·98 |

In an experiment to ascertain whether all the moisture was removed by drying in vacuo over  $\text{SO}_3$ , a quantity of about two grammes by exposure to a temperature of 210° to 212° for 9 hours in the exsiccator lost a little less than one and a half milligrammes.

Heated on platinum foil the ammonia picrate of copper explodes with some violence and with a dazzling light.

*Ammonia-picrate of Cobalt.*

To a solution of protochlorid of cobalt prepared from chlorid of purpureo-cobalt in the manner recommended by Gibbs and Gen'th in their interesting and valuable paper on the ammonia-cobalt bases, a large excess of ammonia was added, and to the filtrate, cold saturated solution of picrate of ammonia. An abundant highly crystalline precipitate falls at once, which after drying is yellowish green: while moist decomposes with great facility with separation of cobaltous oxyd.

|                      |                                |
|----------------------|--------------------------------|
| ·6293 substance gave | ·4784 picric acid.             |
| ·6075 " "            | ·4594 " "                      |
| ·6067 " "            | ·1641 protosulphate of cobalt. |
| ·5416 " "            | ·1475 " " "                    |
| ·6075 " "            | ·2065 chlorhydrate of ammonia. |

which results lead to the formula:—

|                                                                               | Calculated.  | Found. |       | Mean. |
|-------------------------------------------------------------------------------|--------------|--------|-------|-------|
|                                                                               |              | 1.     | 2.    |       |
| $2\text{NH}_3\text{CoO} \cdot \text{C}_{12}\text{H}_2\text{N}_3\text{O}_{14}$ | 75·87        | 75·69  | 75·29 | 75·49 |
| Co                                                                            | 9·82         | 10·13  | 10·29 | 10·21 |
| $2\text{NH}_3$                                                                | 11·32        | 10·81  |       | 10·81 |
| HO                                                                            | 2·99         |        |       |       |
|                                                                               | <hr/> 100·00 |        |       |       |

This salt is much more unstable than the foregoing, and undergoes a commencement of decomposition in washing: even when this part of the operation is performed with great care, using carbonate of ammonia and dilute liquid ammonia, a portion of picrate of ammonia is washed through, and as cobaltous oxyd is not easily soluble in ammoniacal solutions, it is not easily removed by washing with such. It is also probable that more or less cobaltous oxyd is thrown down with the precipitate, as the latter at the first moment crystalline, becomes quickly more and more curdy—and ammoniacal solution of cobalt by mere dilution with water throws down a bright green precipitate. In the preparation of the ammoniacal solution, it is better to drop a strong solution of cobaltous chlorid into a large excess of ammonia.

Like the foregoing this salt explodes by heat.

*Ammonia-picrate of Zinc.*

To a solution of pure sulphate of zinc, chlorhydric acid was added in sufficient quantity to prevent precipitation by the sub-

sequent addition of ammonia in excess. To the clear solution, a hot, strong solution of picrate of ammonia was added. Immediately the whole became nearly solid with beautiful yellow needles and scales—the beaker was rapidly cooled by cold water, the contents thrown on a filter, and washed first with a solution of carbonate of ammonia mixed with caustic ammonia, and finally with dilute caustic ammonia alone.

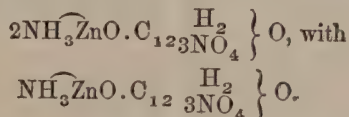
The splendid gold yellow mass of interlaced needles and scales, was more or less decomposed, even by the most careful washing, so that the brightest and purest parts only could be taken for analysis, nor were even these satisfactory.

|                      |                           |              |
|----------------------|---------------------------|--------------|
| $C_{12}H_2N_3O_{14}$ | mean of 5 determinations, | 81.26        |
| $NH_3$               | “ 3 “                     | 9.06         |
| Zn                   | “ “ “ “ “ “               | 10.08        |
|                      |                           | <hr/> 100.30 |

The formula  $3NH_3 \cdot 2 \left[ ZnO \cdot C_{12} \frac{H_2}{3NO_4} \right] O$  requires:—

|                       |   |   |   |   |              |
|-----------------------|---|---|---|---|--------------|
| $2C_{12}H_2N_3O_{14}$ | - | - | - | - | 79.692       |
| $3NH_3$               | - | - | - | - | 8.913        |
| $2Zn$                 | - | - | - | - | 11.395       |
|                       |   |   |   |   | <hr/> 100.00 |

The salt examined may be either this compound containing admixed picrate of ammonia, or may be a mixture of:—



The fact that when a strongly acid solution of zinc-chlorid is supersaturated with ammonia, the compounds  $2NH_3 \cdot ZnO \cdot HCl$  and  $NH_3 \cdot ZnO \cdot HCl$  successively crystallize out, speaks in favor of the latter hypothesis.

#### *Ammonia-picrate of Cadmium.*

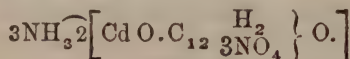
The cadmium salt is obtained and purified in exactly the same manner as the zinc, which it nearly resembles: it is however not so bright in color, but pure canary yellow. Like the zinc salt it redissolves in its mother liquid by heat without decomposition, but like almost all the compounds here described, when washed with pure water on a filter, the picric acid and ammonia wash through. A greyish white residue of oxyd of cadmium remains behind.

Heated on platinum foil, the salt deflagrates with a beautiful green light.



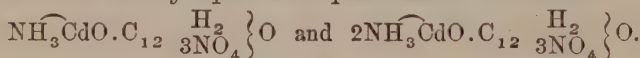
|        |                |       |                            |
|--------|----------------|-------|----------------------------|
| ·7170  | substance gave | ·5247 | picric acid.               |
| ·6622  | "              | ·4877 | " "                        |
| 1·1459 | "              | ·8452 | " "                        |
| ·6496  | "              | ·1653 | sal ammoniac.              |
| 1·1459 | "              | ·2945 | " "                        |
| ·6045  | "              | ·6289 | chlorplatinate of ammonia. |
| ·7321  | "              | ·1501 | cadmium oxyd.              |

These results lead to the formula:—



|                                                                   | Calculated. | 1.    | 2.    | Found. 3. | Mean. |
|-------------------------------------------------------------------|-------------|-------|-------|-----------|-------|
| 2(C <sub>12</sub> H <sub>2</sub> N <sub>3</sub> O <sub>14</sub> ) | 73·67       | 73·44 | 72·86 | 73·31     | 73·20 |
| 3NH <sub>3</sub>                                                  | 8·24        | 8·10  | 8·17  | 7·93      | 8·07  |
| 2Cd                                                               | 18·09       | 17·94 |       |           | 17·94 |
|                                                                   | 100·00      |       |       |           | 99·24 |

It seems however not improbable that this substance may be a mixture in nearly equivalent quantities of the salts:—



for reasons similar to those mentioned in the case of the zinc salt.

### *Ammonia-picrate of Chromium.*

This salt is easily obtained from an ammoniacal solution of chromoxyd which may be prepared in the following manner:

Three grammes of potash chrome alum are dissolved in water by boiling, the solution removed from the fire and 14 c. c. of pure concentrated sulphuric acid and 90 c. c. of liquid ammonia added. A strongly alkaline beautiful purple solution is thus obtained which may be preserved in well stopped vessels quite filled, for a considerable time.\*

To a solution prepared in this manner, a strong hot solution of picrate of ammonia, not in excess, is to be added. Some precipitation follows at once which increases very much as the solution cools. The precipitate is thrown on a filter and washed with dilute liquid ammonia. It consists of splendid green metallic looking scales which if heated with a considerable quantity of water, even strongly ammoniacal, are decomposed with

\* While studying the chromium salt, I met with Frémy's "Investigation of the salts of chromium." In it the author states that the salts of chromoxyd modified by boiling (green modification) are insoluble in ammonia except after having been boiled in acid and precipitated by ammonia. It will be observed that the above process is not in conformity with the opinion of M. Frémy, as it is there shown that the green modification, produced by boiling, is rendered soluble in ammonia by the simple addition of sulphuric acid and without any application of heat. The solution in ammonia is always complete, and the process never fails.

precipitation of chromoxyd. On cooling, picrate of ammonia crystallizes out. Even with very careful washing the salt is always partly decomposed, with separation of green oxyd of chromium.

The portions that were least decomposed were selected, but were not sufficiently pure to give any satisfactory result, although a number of specimens were analyzed.

|    |       |                |       |                     |
|----|-------|----------------|-------|---------------------|
| 1. | ·6949 | substance gave | ·5864 | picric acid.        |
| 2. | ·5537 | " "            | ·4735 | " "                 |
| 3. | ·4446 | " "            | ·3709 | " "                 |
| 4. | ·4446 | " "            | ·0179 | sesq. ox. chromium. |
| 5. | ·6949 | " "            | ·0271 | " "                 |

These numbers correspond to

|    |                      |       |           |
|----|----------------------|-------|-----------|
| 1. | $C_{12}H_2N_3O_{14}$ | 84·02 | per cent. |
| 2. | "                    | 85·14 | " "       |
| 3. | "                    | 83·06 | " "       |
| 4. | Cr                   | 2·78  | " "       |
| 5. | "                    | 2·63  | " "       |

results which do not lead to any satisfactory conclusion, but show that the quantity of ammonia salt necessary to keep the chromoxyd in solution, throws down picrate of ammonia simultaneously with the ammonia-picrate of chromium. This salt is very beautiful, its lustre is remarkable.

#### *Ammonia-picrate of Manganese.*

If ammonia be added to a solution of manganous sulphate, previously rendered strongly acid with chlorhydric or nitric acid, a considerable quantity of manganese escapes precipitation, an extremely unstable solution is obtained, which in a few minutes, even before filtration is ended, becomes cloudy again. To give the solution more stability, the presence of a very large quantity of ammonia salt is necessary, a circumstance very unfavorable for the production of a pure ammonia-picrate, as by a solution so strongly saline, picrate of ammonia (as already observed) is at once precipitated. The following were the observations made:—

A. If a cold solution of picrate of ammonia be poured into an ammoniacal solution of manganese prepared by adding to a concentrated solution of manganous sulphate an equal volume of dilute chlorhydric acid, and then ammonia in large excess, there falls a precipitate of brilliant satiny scales, mixed however with precipitated manganous oxyd, which is readily distinguishable on the filter.

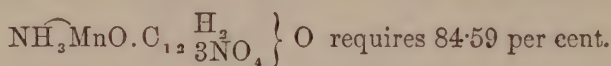
B. If the ammoniacal solution is added to a hot moderately strong solution of picrate of ammonia and the whole be rapidly

filtered, the liquid passes through before complete precipitation takes place, and on cooling, granular crystals are obtained which rapidly turn brown in the air. Heated on platinum foil, they turn brown, melt and deflagrate sharply with a brilliant white light.

Neither A, nor B, yield a salt sufficiently pure for analysis. A, always contains admixed manganous oxyd and B, picrate of ammonia. A, bears considerable resemblance to the chrome salt just described.

1.0115 of B gave .9115 picric acid.

So large a percentage of picric acid corresponding to 89.72 per cent of the molecule  $C_{12}H_2N_3O_{14}$ , probably indicates a large admixture of picrate of ammonia, which cannot be removed. The formula



#### *Ammonia-picrate of Iron.*

An ammonia-picrate of protoxyd of iron appears to exist. If solution of protosulphate of iron be mixed with one of salammoniac, and then with liquid ammonia, be rapidly filtered, and the filtrate be treated with picrate of ammonia, a dark green crystalline precipitate is obtained: thrown upon a filter a red liquid passes through containing a portion of the picrate of ammonia reduced by the ferrous oxyd. The precipitate, when heated on platinum foil, deflagrates with scintillations. Heated with solution of salammoniac and caustic ammonia, it does not appear to dissolve, but ferric oxyd is thrown down and picrate and picramate of ammonia remain in solution. It was found impossible to obtain this salt in a condition to admit of even an approximate determination of its constitution.

If acetate of lead be treated with ammonia in excess, and if to the clear solution be added picrate of ammonia, a curdy precipitate, at first pale yellow, gradually deepening to orange color falls. Heated on platinum foil it detonates with violence. Boiled with caustic alkali, it disengages no ammonia. The result of an analysis showed it to be Marchand's penta-basic picrate of lead,  $4PbO PbO C_{12}\frac{H_2}{3NO_4}\} O$ . The above described salts containing ammonia are all highly crystalline. The lead compound just mentioned is amorphous.

Other ammonia picrates exist which I propose to examine hereafter.

Philadelphia, July 14, 1860



## ON THE FORMATION OF PICRAMIC ACID.

By M. CAREY LEA.

It is to Mr. Aimé Girard that we owe the first isolation of picramic acid, and correct determination of its constitution. His views however of the circumstances under which it is formed do not altogether agree with the results of my observations, and I advert to them now, because his second paper contains a criticism on the results obtained by another chemist, which criticism I think depends upon an inexact view of the reactions.

In a paper published by Dr. Evan Pugh in Liebig's *Annalen*, he endeavored to establish the identity of picramic acid with Wöhler's nitrohæmatic acid. Mr. Girard, while he agrees with Mr. Pugh in his conclusions, rejects his experiments and reasonings as insufficient.

"This chemist, in fact" he says "proceeded exactly as Mr. Wöhler had done before I demonstrated the formation of picramic acid by means of sulphydric acid. His process consists in mixing picric acid with protosulphate of iron, boiling with excess of baryta, precipitating the soluble baryta salt with ammoniacal acetate of lead and *finally in decomposing the lead salt by sulphydric acid*. Now it is evident that under these circumstances, even supposing that the protoxyd of iron had not converted the picric acid to picramic, the sulphydric acid alone would have produced this reduction." \*

At first sight this conclusion seems perfectly legitimate, so much so, that it is probable that no test by experiment was thought necessary. Had such been made it would have been ascertained that sulphydric acid *is wholly without power to reduce picric acid whether free or in combination with lead, to picramic acid*.

The fact appears to have been overlooked that sulphydric acid is quite incapable of producing this reaction either upon picric acid, or as far as my experiments go, upon any picrate. It is the alkaline sulphids that possess this power, and not free sulphydric acid, a circumstance which has not been noticed, in consequence of chemists operating on solutions of picric acid in alcohol to which excess of ammonia had been added. When sulphydric acid is passed through such a solution, sulphhydrate of ammonia is formed and acts on the picric acid.

Sulphydric acid may be passed through solutions of picric acid, picrate of potash or picrate of ammonia, either at ordinary temperatures, or at a boiling heat, for any length of time, without producing the slightest effect. On the addition of excess of alkali the reducing effect of the sulphid formed is immediate.

Philadelphia, Nov. 30, 1860.

# REMARKS ON A PROPOSED PROCESS FOR THE ESTIMATION OF NITROGEN, AND ON AN ACIDIMETRIC PROCESS.

BY M. CAREY LEA.

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IN a late number of the London Chemical News\* a modification of Will and Varrentrapp's process for the estimation of nitrogen is proposed by Mr. J. Walker. He decomposes the substance in a combustion tube in the ordinary way, but instead of conducting the products of the combustion into chlorhydric acid, conducts them into solution of chlorid of zinc, and in place of determining the ammonia in the usual manner, determines the amount of oxyd of zinc precipitated by it. "This process," the author observes, "has been practised by me for the last two years, and gives most accurate results, and I can with perfect confidence recommend it."

Few chemists would be apt to adopt a process so obviously worthless, but as its author recommends it especially for the analysis of manures, and as in that way it might be employed for technical purposes, it seems desirable that its gross inaccuracy should be pointed out. Oxyd of zinc is well known to be easily soluble in ammonia salts: if a drop of caustic ammonia is let to fall into a solution of pure neutral chlorid of zinc, it occasions a precipitate of oxyd, if now solution of sal-ammoniac be added, the precipitate redissolves. Obviously if more ammonia, instead of sal-ammoniac, is added, sal-ammoniac is formed by the decomposition of the zinc salt, and a portion of the precipitate is redissolved by it, or to speak more correctly, a portion of the oxyd of zinc which is liberated by the ammonia, is held in solution by the sal-ammoniac. The necessary result must be an under-estimation of the ammonia, leading to errors of such magnitude as would render the process wholly unfit even for the roughest technical process.

In consequence of overlooking the frequent solubility in alkaline solutions of certain metallic oxyds and basic salts insoluble in water, even chemists of experience have been led into singular errors. Dr. Friedrich Mohr in his interesting book on Volumetric Analysis, highly recommends a process proposed by Kieffer for acidimetric estimation, and which is briefly as follows. Sulphate of copper in solution is treated with liquid ammonia until the precipitate formed is nearly redissolved; it is then filtered, diluted to a certain strength and constitutes the test liquid. If this be dropped into an acid, or an acid solution, after the addition of a certain quantity a precipitate falls, the appearance of which Kieffer and Dr. Mohr consider to mark the moment

of the exact saturation of the acid liquid by the joint action of the ammonia and copper. Dr. Mohr observes:\*

“*Donc le moindre excès de la liqueur de dosage formera un précipité bien net, tout à fait insoluble dans la dissolution des deux sels complètement neutres.*”†

Here is an important error, this precipitate is by no means insoluble in such solutions, it is soluble with considerable facility in solution of sulphate of ammonia (in the above passage Dr. Mohr refers more particularly to the dosing of sulphuric acid) and also, though to perhaps not to so great an extent, in solutions of sal-ammoniac and of nitrate of ammonia. Consequently when the precipitate appears, it is because the solution is saturated with it. If it were not that the effect of the cupro-ammoniacal solution is directed to be determined empirically and not by calculation, this solubility would have led to discrepancies no doubt sufficiently great to have awakened suspicion. But the error is just sufficiently great to make the process dangerous. More or less of the precipitate is held in solution according as the saline solution is more or less dilute. Consequently if the liquid to be analyzed contains no saline matter, the error may be but trifling, the error in the analysis correcting more or less accurately the original error in the determination of the “titre.” This mode of estimation is particularly recommended for determining the quantity of free acid in acid saline solutions, but here is just where it would be most fallible, the nature and quantity of the saline substance in solution exerting a powerful influence on the solubility of the precipitate. It is evident that a solution containing 5 grammes of free sulphuric acid with 5 grammes of sulphate of ammonia, tested in this way, would give quite a different result from one in which 5 grammes of free acid was contained with 20 or 50 of sulphate of ammonia. Likewise its results when used in the “method of residues” must be false. Accordingly in an experimental trial by Dr. Mohr‡ for the determination of magnesia by supersaturation with a known quantity of sulphuric acid, and determination of the residue of uncombined acid, the result which he obtained is erroneous by 4 per cent. Four per cent too little of magnesia were obtained, because the free sulphuric acid was over-estimated, the ammonio-cupric solution having been added till a precipitate was obtained, which as we have just seen, does not fall till *after* the saturation point has been reached.

The precipitate which appears in all these cases is spoken of by Dr. Mohr as hydrated oxyd of copper. It appears to be basic (probably quadrobasic) sulphate.

\* Not having a German copy at hand I quote from the French translation made by Forthomme under the superintendence of Dr. Mohr.

† Forthomme's translation, p. 409.

‡ Op. cit., p. 412.



In making these observations on a single process of Dr. Mohr, I wish at the same time to bear testimony as to the candor with which he has given the results of his experimental trials. The proposal of a mode of analysis such as that of Mr. Walker is a new proof how much it is to be regretted that any chemist should offer a new mode of analysis, without having first controlled it by the analysis of one or more specimens of substance of a known composition. In this way MM. Glénard and Guillemond have recently proposed\* a method of estimating the quinine in barks. It has been however shown† that not only the presence of cinchonine destroyed the accuracy of these results, but that owing to a mistake of the authors as to the reaction of the sulphates of quinine upon tincture of logwood, the process when performed with pure quinine gave only one-half the true result.

In connection with the foregoing observations on zinc I may remark that an error has crept into the description of zinc reactions in Gmelin's Handbook. It is there stated that zinc salts give precipitates with ferrocyanid and ferridcyanid of potassium, both of which are soluble in chlorhydric acid.‡ As respects the precipitate with ferrocyanid, this is certainly erroneous, the precipitate does not redissolve in that acid.

Philadelphia, Dec. 28, 1860.

\* Rep. de Chimie Appliquée, 1859, p. 131.

† Idem, 1860, p. 61.

‡ Handbook, vol. v, p. 12, Cavendish edition.

# CRYSTALLINE FORM

NOT NECESSARILY AN

## INDICATION OF DEFINITE CHEMICAL COMPOSITION;

OR, ON THE POSSIBLE VARIATION OF CONSTITUTION

IN A MINERAL SPECIES

INDEPENDENT OF THE PHÆNOMENA OF ISOMORPHISM.

BY

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IN a memoir presented to the American Academy of Arts and Sciences in September 1855\*, I described two new compounds of zinc and antimony, which I named *stibiobizincyle* and *stibiotrizincyle*, on account of their analogy in composition to the metallic radicals of organic chemistry. The symbols of these compounds are  $\text{Sb Zn}^2$  and  $\text{Sb Zn}^3$ ; and they are distinguished by the high perfection of their crystalline forms, the last being still further characterized by a most remarkable property of decomposing water quite rapidly at  $100^\circ\text{C}$ . I stated in the same memoir that crystals of these two compounds could be obtained, containing proportions of zinc and antimony differing very widely from those required by the law of definite proportions; and I also traced out the relation between the composition of the crystals, and that of the menstruum in which they are formed. It is my object in the present paper to consider the bearing of these facts, already fully described, on the idea of mineral species, and to offer a few suggestions which I hope may be of service in determining the true chemical formulæ of many minerals, and thus in simplifying the science of mineralogy. But in order to render myself intelligible, it will be necessary to recapitulate very briefly the facts in question, referring to the original memoir for the full details.

\* Transactions of the American Academy of Arts and Sciences, New Series, vol. v. p. 337.

The crystals both of  $\text{Sb Zn}^2$  and  $\text{Sb Zn}^3$  can be obtained with great readiness. It is only necessary to melt together the two metals in the atomic proportions, and when the metals are fully alloyed, to proceed exactly as in crystallizing sulphur. The melted mass is allowed to cool until a crust forms on the surface, which is then broken, and the liquid metal remaining in the interior poured out. On subsequently breaking the crucible, the interior is found lined with magnificent metallic crystals, which, when not tarnished by oxidation, have a silver-white lustre. In the course of my investigations on these compounds, crystallizations were made, or attempted, of alloys differing in composition by one half to five per cent., according to circumstances, from the alloy containing 95 per cent. of zinc, to that containing 95 per cent. of antimony; *but only two crystalline forms were observed*, that of  $\text{Sb Zn}^2$  and that of  $\text{Sb Zn}^3$ . The crystals of the two compounds both belong to the trimetric system; but they differ from each other, not only in their crystallographic elements, but also in their whole "habitus." Stibiotrizincyle crystallizes in long acicular prisms, which group themselves together into larger prismatic aggregates; while stibiobizincyle crystallizes in broad plates, which twin together on an octahedral face, and form a very characteristic cellular structure. This very striking difference in the character of the crystals proved to be an important circumstance in the investigation, as it enabled me to distinguish with certainty between the two compounds, even when the faces of the crystals were so imperfect that a measurement of angles was impossible.

The most remarkable result of the investigation, and the one to which I wish to direct especial attention, is the fact that each of the two crystalline forms was found to be constant under very wide variations in the per-centage composition of the crystals. As this is a point of great importance, it will be necessary to enter more into detail, considering in the first place the crystals of  $\text{Sb Zn}^3$ . The crystals of this compound are obtained in the greatest perfection from an alloy containing the two metals in just the proportions represented by the formula, namely, 42·8 parts of zinc, and 57·2 parts of antimony. They are then comparatively large, generally aggregated, and, as the three analyses cited in the accompanying Table indicate, they have the same composition as the alloy.

| Composition of the alloy by synthesis. |                  | Composition of the crystals by analysis. |                  |        |
|----------------------------------------|------------------|------------------------------------------|------------------|--------|
| Per cent. of Zn.                       | Per cent. of Sb. | Per cent. of Zn                          | Per cent. of Sb. | Sum.   |
| 42·80                                  | 58·20            | 43·15                                    | 56·93            | 100·08 |
| "                                      | "                | 43·06                                    | 56·50            | 99·56  |
| "                                      | "                | 42·83                                    | 57·24            | 100·07 |



On increasing gradually the amount of zinc in the alloy up to 48.7, the crystals continued to have the composition of the alloy; and the only difference which could be observed in their character was that they were smaller, and more frequently isolated. Between these limits the whole mass of the alloy exhibited a strong tendency to crystallization; and by pouring it, as it cooled, from one vessel to another, it could be crystallized to the last drop. On increasing the amount of zinc in the alloy to 50.7 per cent., the amount of zinc found in the crystals was uniformly less than it was in the alloy; but no closer relation between the two could be detected, owing, undoubtedly, to the unavoidable irregularity in the crystallization of the alloys which contained more than 50 per cent. of zinc. This arose from a peculiar pasty condition which the liquid mass assumed at the point of crystallization. Definite crystals, however, were obtained from an alloy of 60 per cent. zinc containing 55 per cent.; above this the crystals became less and less abundant, and gradually faded out, although the alloy of 86 per cent. of zinc exhibited a radiated crystalline texture; and a trace of this structure could still be discovered even in the alloy containing only 4 per cent. of antimony. It was very interesting to trace the gradual fading out of the crystalline structure, as the character of the phenomenon was entirely analogous to that which may be noticed in many crystalline rocks.

Finding that the crystalline form of  $\text{Sb Zn}^3$  was constant under so great an increase of the proportion of zinc in the crystals, it might be supposed that, on returning to the alloy of 42.8 per cent. of zinc and increasing the amount of antimony, we should obtain crystals containing an excess of antimony; but so far is this from being true, that the slightest excess of antimony entirely changes the character of the crystallization. On crystallizing an alloy containing 41.8 per cent. of zinc, not a trace of any prismatic crystals could be seen; but in their place there was found a confused mass of thin metallic scales, which, as will soon be shown, are imperfect crystals of  $\text{Sb Zn}^2$ . Thus it appears that, although perfectly formed crystals of  $\text{Sb Zn}^3$  can be obtained containing 55 per cent. of zinc (that is, 12 per cent. above the typical proportions), they cannot be made to take up the slightest excess of antimony.

Let us pass now to the crystals of  $\text{Sb Zn}^2$ . In order to obtain crystals having the exact typical constitution, it was found necessary to crystallize an alloy at least as low as 31.5 per cent. of zinc. At this point large compound crystals are obtained corresponding to the large crystals of  $\text{Sb Zn}^3$ ; and the same was true of alloys down to 27 per cent. of zinc. Between these two limits (namely, alloys of 31.5 and 27 per cent. of zinc) the cry-

stals formed were found to have the theoretical composition of  $\text{Sb Zn}^2$ , indicating of course a tendency towards this point; but on increasing or diminishing the amount of zinc in the alloy beyond these limits, the composition of the crystals immediately began to vary in the same direction as that of the alloy. The crystals of  $\text{Sb Zn}^2$  containing an excess of zinc are smaller and more frequently isolated than those having the exact theoretical composition. A similar fact, it will be remembered, is true of the crystals of  $\text{Sb Zn}^3$ .

At the alloy of 33 per cent. of zinc, the definite crystals of  $\text{Sb Zn}^2$  begin to disappear, and are succeeded by thin metallic scales, which are obviously imperfect crystals of the same form. This was established, not only by the obvious law of continuity noticed in the different specimens (the perfect crystals gradually passing into the scales), but also by the peculiar mode of twinning, which was the same with the scales as with the large crystals, forming the peculiar cellular structure already referred to. Moreover, the angle between two scales thus united was found to be equal to the basal angle of the perfect crystals, at least as nearly as could be measured. These scales continue up to the alloy of 41.8 per cent. of zinc, becoming, however, less abundant and less distinct. Several specimens of them were analysed; but no regularity could be detected in their composition, except that they all contained a much larger amount of zinc than the alloys in which they were formed.

Crystals of  $\text{Sb Zn}^2$  containing an excess of antimony were readily obtained from alloys containing less than 27 per cent. of zinc. They became more and more imperfect as the excess of antimony increased, and finally faded out altogether in the alloys below 20 per cent. of zinc. It is evident, therefore, that definite and perfect crystals of  $\text{Sb Zn}^2$  can be obtained with a large excess either of zinc or antimony above the theoretical composition. It is also evident that, of the two compounds,  $\text{Sb Zn}^2$  is the most stable,—first, because it is formed to the exclusion of  $\text{Sb Zn}^3$  in all alloys containing less zinc than the amount corresponding to the typical composition of the last compound; and secondly, because the crystals retain the typical composition under quite a wide variation (viz. between 31.5 and 27 per cent.) in the composition of the alloy.

The facts above stated are fully illustrated by the following Table, which gives the results of a large number of analyses of crystals of both compounds formed in alloys containing different proportions of the two metals:—

# Analyses of the Crystals formed in the Alloys of Zinc and Antimony.

| Stibiotrizineyle.                       |                  |                                          |                  |         | Stibiobizineyle.                        |                  |                                          |                  |         |
|-----------------------------------------|------------------|------------------------------------------|------------------|---------|-----------------------------------------|------------------|------------------------------------------|------------------|---------|
| Composition of the alloys by synthesis. |                  | Composition of the crystals by analysis. |                  |         | Composition of the alloys by synthesis. |                  | Composition of the crystals by analysis. |                  |         |
| Per cent. of Zn.                        | Per cent. of Sb. | Per cent. of Zn.                         | Per cent. of Sb. | Sum.    | Per cent. of Zn.                        | Per cent. of Sb. | Per cent. of Zn.                         | Per cent. of Sb. | Sum.    |
| 70.40                                   | 29.60            | 64.15                                    | 35.77            | 99.92   | 33.00                                   | 67.00            | 35.37                                    | 64.57            | 99.94   |
| 66.50                                   | 33.50            | 61.00                                    | 39.00            | *100.00 | 33.00                                   | 67.00            | 35.40                                    | 64.60            | †100.00 |
| 64.50                                   | 35.50            | 53.50                                    | 41.44            | 99.94   | 32.50                                   | 67.50            | 34.62                                    | 64.92            | 99.54   |
| .....                                   | .....            | 55.49                                    | 44.42            | 99.91   | 32.50                                   | 67.50            | 34.61                                    | 65.39            | †100.00 |
| 60.60                                   | 39.40            | 55.00                                    | 45.09            | 100.09  | 31.50                                   | 68.50            | 33.95                                    | 66.09            | 100.04  |
| 58.60                                   | 41.40            | 50.39                                    | 49.29            | 99.68   | 29.50                                   | 70.50            | 33.62                                    | 66.38            | †100.00 |
| 56.60                                   | 43.40            | 49.92                                    | 50.05            | 99.97   | 29.50                                   | 70.50            | 33.62                                    | 66.38            | †100.00 |
| 54.70                                   | 45.30            | 48.26                                    | 51.42            | 99.68   | 27.50                                   | 72.50            | 33.85                                    | 65.81            | 99.66   |
| 52.70                                   | 47.30            | 47.47                                    | 52.53            | †100.00 | 26.50                                   | 73.50            | 32.08                                    | 67.60            | 99.68   |
| .....                                   | .....            | .....                                    | .....            | .....   | 26.00                                   | 74.00            | 30.74                                    | 69.06            | 99.80   |
| 50.70                                   | 49.30            | 46.89                                    | 53.11            | †100.00 | 25.50                                   | 74.50            | 30.43                                    | 69.51            | 99.94   |
| 50.70                                   | 49.30            | 46.45                                    | 53.55            | †100.00 | 25.00                                   | 75.00            | 29.88                                    | 70.20            | 100.08  |
| 48.70                                   | 51.30            | 48.66                                    | 51.34            | †100.00 | 24.50                                   | 75.50            | 28.76                                    | 71.24            | 100.00  |
| 46.70                                   | 53.30            | 46.77                                    | 53.23            | †100.00 | 23.50                                   | 76.50            | 27.93                                    | 71.85            | 99.78   |
| 44.80                                   | 55.20            | 44.26                                    | 55.73            | †100.00 | 22.50                                   | 77.50            | 26.62                                    | 73.27            | 99.89   |
| 43.80                                   | 56.20            | 44.04                                    | 55.96            | †100.00 | 21.50                                   | 78.50            | 24.83                                    | 74.74            | 99.57   |
| 42.80                                   | 58.20            | 43.15                                    | 56.93            | 100.08  | 20.12                                   | 79.88            | 20.58                                    | 79.42            | 100.00  |
| 42.80                                   | 58.20            | 43.06                                    | 56.50            | 99.56   |                                         |                  |                                          |                  |         |
| 42.80                                   | 58.20            | 42.83                                    | 57.24            | 100.07  |                                         |                  |                                          |                  |         |

\* In this analysis the antimony only was determined.

† In this analysis the zinc only was determined.

The relation between the composition of the crystals  $\text{Sb Zn}^2$  and that of the alloy in which they are formed, is discussed at length in the memoir already referred to. It is there shown to be a very simple function of the mass of metal which is in excess in the alloy, and of the force which determines the union of the elements in definite proportions. The whole order of these phenomena seem to the author to point to the existence of a power in the mass of metal which is in excess in the alloy, to disturb the action of the force, whatever it may be, which tends to unite the elements in definite proportions. There is, in the first place, a strong tendency in the elements to unite and form crystals having the exact typical composition; and secondly, this tendency is only overcome by a certain excess of either metal in the alloy. Then, again, the crystals of one compound obviously interfere with those of the other. This certainly has the appearance of one force interfering with the action of another, —the force of mass (if I may so call it) perturbing the action of the chemical force. But it is not my object at present to enter into a discussion on the cause of this variation. Moreover, since



such a discussion must be based on purely hypothetical grounds, we could not expect to arrive at any definite conclusion. The facts will be viewed differently according to the theory which may be adopted in regard to that long-controverted subject, the essential constitution of matter. Leaving, however, all theoretical considerations aside, there are certain practical bearings of the *observed facts* on the science of mineralogy which are of immediate application.

Here are two beautifully crystallized products, as well crystallized as any that occur in nature, and yet the different specimens of the crystals differ from each other so widely in composition that any single analysis might lead to an entirely erroneous conclusion in regard to the general formula of the substance. Were a chemist to analyse accidentally solely the crystals obtained from an alloy containing 58·6 per cent. of zinc, he would at once determine that the formula of the compound was  $\text{Sb Zn}^4$ ; and by a like accident he might be led to any other formula between this and  $\text{Sb Zn}^3$ : in fact, by an analysis of a number of specimens of needle-shaped crystals obtained from alloys of copper and tin, Rieffel was led to several just such improbable formulæ; and in my own investigations it was not until I had analysed a whole series of crystals, that the real nature of the phenomena became apparent, and the true constitution of the compounds determined. If, then, such great variations in composition are compatible with a definite crystalline form in these furnace products, may not similar variations occur in the crystalline minerals formed in nature?

It is not necessary to make an extended investigation in order to answer this question; for the materials at our hands are sufficient to give us a satisfactory reply.

There is a compound of antimony and silver called Discrasite, which occurs in many localities crystallized in trimetric prisms homœomorphous with  $\text{Sb Zn}^3$ . The formula of the mineral is therefore probably  $\text{Sb Ag}^3$ , which would require 71·5 per cent. of silver; but the per cent. as given by analysis varies between 75·25 and 78 per cent., and one analysis gives the per cent. as high as 85. Further analyses of this mineral are required in order to determine its constitution, but there can be no doubt that it varies in composition like  $\text{Sb Zn}^3$ .

Silver-glance is another highly crystalline mineral. Theoretically it should contain 87·1 per cent. of silver and 12·9 per cent. of sulphur; but in a specimen analysed by Klaproth, the proportions were 85 and 15.

Again, the analyses of pyrrhotine (magnetic pyrites) give results varying between 38·78 per cent. sulphur, 60·52 per cent. iron (variety from Bodenmais), and 43·63 sulphur, 56·37 iron

(variety from Barèges). The constitution of the mineral is still uncertain; but its true formula is probably  $\text{FeS}$ , which would require 36.4 per cent. sulphur and 63.6 per cent. iron. Lastly, the analyses of antimony-glance give results varying between

|                 |     |                |
|-----------------|-----|----------------|
| Antimony 74.06, | and | Antimony 73.5, |
| Sulphur 25.94,  |     | Sulphur 26.5.  |

The true formula of this mineral is undoubtedly  $\text{SbS}^3$ , which would require only 72.88 per cent. of antimony.

Similar examples might be very greatly multiplied. Those just cited were selected at random from the first few pages of Dana's 'System of Mineralogy.' They are all examples of binary compounds which occur almost chemically pure in nature; so that the phenomena in question are not complicated by those of isomorphism.

When we pass to minerals of more complex constitution, the same phenomena can be made evident, although not quite so easily, on account of the introduction of the phenomena of substitution by isomorphous elements. It will not, however, be necessary for me to cite examples; for it is a fact perfectly well known to all mineralogists, that, after making allowances for the substitution of isomorphous elements, the various analyses of such minerals as mica, hornblende, garnet, and tourmaline differ very greatly from each other,—a difference, moreover, which no mere error of analysis will explain, and which must therefore be referred to an actual variation in composition. In the silicates this variation in composition is made evident by the variation of what is termed the "oxygen ratios;" and it is well known to mineralogists that in many species this variation is very large. For example, in mica the following ratios between the oxygen in the base and acid have been observed in merely the Muscovite variety:— $13:16$ ,  $13\frac{1}{2}:16$ , and  $14\frac{2}{3}:16$ ; and similarly wide variations might be pointed out in other well-known species. It is in consequence of such variations as these that the general chemical formulæ of some of the best-known mineral species, such as mica and tourmaline, are still uncertain; and in other cases, where the true formula is probably known, the constitution of the mineral has been determined quite as much from other considerations as from the chemical analyses.

Sufficient has been said, I think, to show that variations in composition similar to those which I have observed in zinc and antimony occur in many minerals; and I trust that the results of my investigation will serve to throw light on this whole class of phenomena, which have so greatly perplexed mineralogists, and rendered all strictly chemical classifications of mineral species so unsatisfactory. This investigation has shown that a defi-

nite crystalline form is compatible with quite a wide variation of composition, and has in this way pointed out an explanation of the variation observed in the mineral kingdom. But more than this, the investigation has also indicated a method by which, amidst all this variation, the true constitution of the mineral can be determined.

In the compounds of zinc and antimony, although the definite crystalline form was compatible with a wide variation in the proportions of the constituent elements, yet the point corresponding to the typical composition was marked by several unmistakeable properties, which clearly enough indicated the true formulæ of the compounds. These properties are discussed at length in my original memoir, and need therefore only to be alluded to in this connexion.

It has already been stated that the crystals, both of  $\text{Sb Zn}^3$  and  $\text{Sb Zn}^2$ , having the theoretical composition are, as a rule, larger and more generally aggregated than those containing an excess of either metal. Moreover, in  $\text{Sb Zn}^2$  the general character of the crystals appears to be modified by the change of composition, although the crystallographic elements remain the same. Thus in the crystals having the theoretical composition, the octahedral planes are greatly developed, giving to the crystals the general appearance of a truncated octahedron\*. But as the crystals take up an excess either of antimony or zinc, the basal planes become more and more dominant, and the crystals are at last reduced to thin plates. In fact, so marked are these changes, that, after a little experience, a person could tell the approximate composition of the crystals from their general appearance. Similar changes in the appearance of many minerals are familiar to the mineralogist. They are seen in calcite, heavy spar, Angle-site, and others, and may serve as guides in tracing variations of composition.

Again, the specific gravity of the crystals, both of  $\text{Sb Zn}^2$  and  $\text{Sb Zn}^3$ , was taken with great care through the whole series, and the results are tabulated below. The union of the two elements is attended with an increase of volume, and this increase is at a maximum at the points corresponding to the theoretical composition. These points would therefore be marked in a set of crystals by being points of minimum specific gravity; and they could be determined with great accuracy by means of this property, even in a series of alloys of the two metals which had not been crystallized. This fact is illustrated by the following Table, reprinted from the original memoir.

\* See figure accompanying my original memoir.



Specific Gravities of Crystals formed in the Alloys of Zinc and Antimony.

| Composition of the alloys. |                  | Composition of the crystals. |                  | Spec. grav. of crystals by experiment. | Mean spec. grav. of zinc and antimony. | Expansion in crystallizing. |
|----------------------------|------------------|------------------------------|------------------|----------------------------------------|----------------------------------------|-----------------------------|
| Per cent. of Zn.           | Per cent. of Sb. | Per cent. of Zn.             | Per cent. of Sb. |                                        |                                        |                             |
| 100.00                     | .....            | .....                        | .....            | 7.153                                  | 7.153                                  | 0.000                       |
| *96.00                     | 4.00             | .....                        | .....            | 7.069                                  | 7.133                                  | 0.064                       |
| *86.20                     | 13.80            | .....                        | .....            | 6.898                                  | 7.082                                  | 0.184                       |
| *76.30                     | 23.70            | .....                        | .....            | 6.769                                  | 7.032                                  | 0.263                       |
| 70.40                      | 29.60            | 64.20                        | 35.80            | 6.699                                  | 6.975                                  | 0.276                       |
| 66.50                      | 33.50            | 61.00                        | 39.00            | 6.628                                  | 6.959                                  | 0.331                       |
| 64.50                      | 35.50            | 58.56                        | 41.44            | 6.596                                  | 6.948                                  | 0.352                       |
| 62.50                      | 37.50            | 55.53                        | 44.47            | 6.506                                  | 6.933                                  | 0.427                       |
| 60.60                      | 39.40            | 55.00                        | 45.00            | 6.440                                  | 6.931                                  | 0.491                       |
| 58.60                      | 41.40            | 50.39                        | 49.61            | 6.396                                  | 6.909                                  | 0.513                       |
| 56.60                      | 43.40            | 49.95                        | 50.05            | 6.388                                  | 6.906                                  | 0.518                       |
| 48.70                      | 51.30            | 48.66                        | 51.34            | 6.404                                  | 6.900                                  | 0.496                       |
| 46.70                      | 53.30            | 46.77                        | 53.23            | 6.376                                  | 6.891                                  | 0.515                       |
| 44.80                      | 55.20            | 44.26                        | 55.74            | 6.341                                  | 6.879                                  | 0.538                       |
| †42.80                     | 57.20            | 43.09                        | 56.91            | 6.327                                  | 6.874                                  | 0.547                       |
| *40.00                     | 60.00            | .....                        | .....            | 6.386                                  | 6.860                                  | 0.474                       |
| *35.00                     | 65.00            | .....                        | .....            | 6.404                                  | 6.837                                  | 0.433                       |
| 33.00                      | 67.00            | 35.37                        | 64.63            | 6.401                                  | 6.838                                  | 0.437                       |
| †29.50                     | 70.50            | 33.62                        | 66.38            | 6.384                                  | 6.830                                  | 0.446                       |
| †27.50                     | 72.50            | 33.85                        | 66.15            | 6.383                                  | 6.831                                  | 0.448                       |
| 26.50                      | 73.50            | 32.08                        | 67.92            | 6.400                                  | 6.822                                  | 0.422                       |
| 26.00                      | 74.00            | 31.07                        | 68.93            | 6.418                                  | 6.818                                  | 0.400                       |
| 25.50                      | 74.50            | 30.43                        | 69.57            | 6.428                                  | 6.816                                  | 0.388                       |
| 24.50                      | 75.50            | 28.76                        | 71.24            | 6.449                                  | 6.807                                  | 0.358                       |
| 22.50                      | 77.50            | 26.62                        | 73.38            | 6.453                                  | 6.798                                  | 0.345                       |
| 21.50                      | 78.50            | 24.83                        | 75.17            | 6.467                                  | 6.790                                  | 0.323                       |
| *15.00                     | 85.00            | .....                        | .....            | 6.564                                  | 6.744                                  | 0.180                       |
| *10.00                     | 90.00            | .....                        | .....            | 6.603                                  | 6.721                                  | 0.118                       |
| *5.00                      | 95.00            | .....                        | .....            | 6.655                                  | 6.698                                  | 0.043                       |
| .....                      | 100.00           | .....                        | .....            | 6.677                                  | 6.677                                  | 0.000                       |

\* Alloys not crystallized.

† Point of typical composition of  $\text{Sb Zn}^3$ .

‡ Point of typical composition of  $\text{Sb Zn}^2$ .

The point of typical composition in the case of the crystals of  $\text{Sb Zn}^3$  was still further marked in a most decided manner by a very remarkable property. It has already been stated that this compound has the power of decomposing water with rapidity at  $100^\circ \text{C}$ .; but this is true only of those crystals which have approximately the theoretical composition. During the course of my investigation I determined the quantity of hydrogen evolved by alloys of different composition during a given time, taking care, of course, that the circumstances should be the same in all cases; and I found that with the alloy containing 43 per cent. of zinc, there is an immense maximum, confined at most between 2 per cent. on either side, the alloy of 43 per cent. yielding over

nine times as much gas as an alloy of 50 per cent., although the crystals of the last were fully as definite as those of the first\*.

It is evident from the above facts, that the points corresponding to the theoretical composition of the two compounds of zinc and antimony, are also *points of maxima and minima* of various properties. Now I have no doubt that the same truth will be found to hold in the mineral kingdom. In a mineral like tourmaline or mica, for example, the specimen having the exact theoretical composition may probably be discovered by examining a large number of specimens, and discussing their various physical properties. All the physical properties may be of value in this connexion, such as lustre, hardness, specific gravity, specific heat, &c.; and no mechanical rules can be laid down. Much must depend on the discretion of the observer; and in any cases such properties will be selected as are best adapted to the circumstances of the case. In comparing different crystals of the same mineral, it is obviously important to select such as have been formed in a different matrix; for it is only with such that we should be led to expect great variations of composition. It is also evident that the phænomena would be complicated when there has been a substitution of isomorphous elements; and until the effect of such substitution on the physical properties can be traced, it will be necessary to select specimens of as uniform a constitution as possible.

With one other consideration I will close this paper. The principle which has been here discussed must modify materially our notion of a mineral species. The idea of a mineral species has hitherto involved chiefly two distinct characters:—first, a definite crystalline form; second, a constant general formula; and any important variation in either of these characters has been regarded as equivalent to a change of species. Rutile and anatase are regarded as different species, because their crystalline forms are slightly different, although both minerals have identically the same constitution; and again, magnetite and Franklinite, which have the same form, are regarded as different species, because they have a slightly different composition. It is true that the actual composition of a mineral may vary very greatly by the substitution of isomorphous elements, and yet, if the general formula remains constant, the species may not be changed. But the extent to which such substitution can be carried without changing the species is not so well settled among mineralogists as could be desired, and the same rule is not applied to all species. The difference between the *varieties* of garnet, for example, is as great as that between the *species* magnetite and Franklinite. Leaving, however, this point undetermined, all mineralogists

\* See Table in the memoir before cited.

have agreed that any *essential change* in the *general formula* was inconsistent with the idea of the *same species*. The result, however, of my investigation is to show that the general formula of a mineral species may vary also, or, as I should rather say, the *general formula* is not necessarily the actual formula of each given specimen, but only the *typical formula* of the species towards which the mineral tends, and which it would unquestionably reach if it could be several times recrystallized.

According to this view, the general formula represents not the *actual constitution* of the mineral, but only a certain *typical composition*, which perhaps is never realized with any actual specimen. The fact that the composition of a mineral species may be modified by the substitution of isomorphous elements, was first established by Mitscherlich, and has long been an admitted principle in mineralogy. We must now, as I think, still further expand our idea of a mineral species, and admit that its composition may be modified by an actual variation in the proportions of its constituents. Thus it is that in mineralogy, as in other sciences, we are led to admit the truth of that maxim which every advance in true knowledge seems to verify, "*Natura non facit saltus.*"

While the results of my investigations thus serve to render the idea of a mineral species less definite than before, I cannot but hope that they will tend ultimately to simplify the whole subject of mineralogy; for not only may we expect to reduce the number of mineral species, but also, by simplifying the general formulæ of those which remain, to classify the whole with a greater precision than is now possible. To do this, however, implies a careful revision of the whole subject-matter of mineralogy on the principles above given,—a labour of which few can appreciate the extent, except those who are familiar with the methods of physical research. The work cannot be done by any one person; and it is the chief object of the present paper to call the attention of mineralogists to the importance of the subject.

I have not thought it necessary to dwell in this paper on the obvious distinction between the phænomena here in consideration, and those of isomorphism. It was shown in my previous memoir, that the variation in the composition of the crystals of  $\text{Sb Zn}^3$  and  $\text{Sb Zn}^2$  could not be explained by this principle; and the distinction between the two classes of phænomena has been still further illustrated by a recent investigation on the crystals formed in alloys of copper and zinc, made in my laboratory by Mr. F. H. Storer. These crystals, which are undoubtedly mixtures of isomorphous elements, give no indications whatever of points of typical composition,—thus illustrating not only the characters of an isomorphous mixture, but also the distinction



between such a mixture and a true chemical compound. Admitting, then, the possibility of a variation of composition in a mineral species, independent of the phenomena of isomorphism, it becomes of importance to distinguish this new class of phenomena by a separate term; and I would propose for this purpose the word *Allomerism*. By this word I would designate *a variation in the proportions of the constituents of a crystallized compound without any essential change in the crystalline form*. If, then, we also use the word *typical* to indicate the condition of *definite composition*, we may speak of those specimens of a mineral species which contain an excess of one or the other constituent, as *allomeric variations from the typical composition*. The degree of allomerism would then be measured by the excess of the *allomeric constituent* above the typical composition. Thus the crystals of  $\text{Sb Zn}^3$  containing 42·3 per cent. of zinc would be said to have the typical composition; while those containing 55 per cent. of zinc would be distinguished as an allomeric variety, the degree of allomerism in this instance amounting to 12 per cent., and zinc being the allomeric constituent. In the case of the mineral Discrasite, it is probable that no specimen having the typical composition has yet been analysed. Those specimens whose analyses are given in Dana's 'System of Mineralogy,' are all probably *allomeric varieties* of the mineral, silver being the allomeric constituent, and the degree of allomerism varying from 4 to 7 per cent. It is unnecessary, however, to multiply examples, as the above are sufficient to illustrate the use of the term.

11a

REPORT  
OF  
THE FOURTH ANNIVERSARY MEETING  
OF THE  
CAVENDISH SOCIETY.

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THE Anniversary Meeting of the Cavendish Society for the year 1851 was held at No. 19, Montague Street, Russell Square, on Saturday, the 1st of March, at three o'clock in the afternoon.

The Chair was taken by THOMAS GRAHAM, Esq., F.R.S., PRESIDENT, who called upon the Secretary to read

THE REPORT OF THE COUNCIL.

“ In their last Annual Report the Council referred with satisfaction to the progressive advancement of the Society, as indicated by the increasing number of its Members; and they expressed a hope that a similar extension would be effected during the year which then commenced. Such an extension seemed to be required in order to place the Society upon a safe and permanent basis, and to insure the complete realization of its objects. Considering the greatly increased extent to which the science of Chemistry has been cultivated in this country within the last few years, as compared with former times, it was thought that a considerable accession of Members might be obtained, and it was confidently anticipated, as the published works of the Society became better known, that the advantages resulting from such an Association would be more amply and adequately appreciated.

" The Council, on reviewing the results of the past year's operations, see no cause for discouragement, although they must admit that all that they desired has not been fully attained. The number of Members has undergone a slow but constantly occurring augmentation, and if the aggregate number be still not so great as it is desirable it should be, there is, nevertheless, every reason to believe that the limit to further extension has not been reached.

" A reference to the financial statements of former years will show the annual progress which has been made by the Society. Thus, in March 1849, 556 Members had paid the subscription for the year 1848, and there were besides about 100 from whom the subscription had not been received, making the number of Members 656. In March 1850, the number of Subscribers for 1848 had been augmented to 791, some of whom, however, had previously retired; and the numbers for 1849 were 694 who had paid, and 56 whose subscriptions were due, making the number of Members at that time 750. During the past year, an increase has been effected to about the same extent as that which occurred in the preceding year, the Subscribers for 1848 having been augmented to 885, and those for 1849 to 854. This last number may be considered to represent the extent of the Society at the present time.

" The Members have received the fourth and fifth volumes of GMELIN'S 'Handbook of Chemistry' for the past year, and the Council have pleasure in announcing that DR. WILSON'S work on Cavendish is now ready, and will be immediately distributed to the Subscribers of 1849. It was thought desirable to proceed with as little delay as possible in bringing out the former of these works, of which there remains but one more volume to complete the Inorganic part, and this the Members will receive in the course of the present year. The delay that has attended the publication of the 'Life of Cavendish,' although unavoidable, was regretted by the Council, but they believe it has been more than compensated for by the large amount of interesting matter which the author was enabled to collect whilst seeking for some of the details of the biography without which he was unwilling to send his work before the public. The characteristic portrait of Cavendish, which forms the frontispiece to the book, has been obtained through the instrumentality of a Member of the Society, Mr. Tomlinson.



It is copied from a drawing, by Alexander, in the print-room of the British Museum, and is considered, by those who knew the philosopher, to be a good and striking likeness. These accessions of matter have not only enhanced the value of the work as a literary production, they have also added to the expenses of publication,—a result which makes it necessary to limit the works issued for 1850 to the two volumes of Gmelin's Chemistry, now in the hands of Members.

“There are several works in course of preparation, to be published in this or succeeding years.

“The first volume of the translation of Lehmann's Physiological Chemistry, by Dr. Day, is now in the hands of the printer, and this will be the first of the books to be issued for 1851. It will be followed by the sixth volume of Gmelin's Chemistry, which will conclude the Inorganic part of this work. The Organic part will then be immediately proceeded with.

“The translation of the Essays of Saussure is prepared, and the abstracts of the works of Hales, Ingenhouz, Sennebier, Wiegmann, and other contemporaneous writers on the chemistry of vegetation, are nearly completed.

“Some of the Members have expressed a desire that the translation of Bischof's Elements of Chemical and Physical Geology, which is among the works proposed for publication by the Society, should be commenced at an early period, but the Council have not, hitherto, found it practicable to make arrangements to this effect without retarding the completion of books previously undertaken.

“It has been suggested to the Council, that a valuable work, for the use of practical chemists, might be prepared through the co-operation of the Members of this Society. Most men engaged in scientific investigations, have occasion to refer to tables for facilitating the calculation of results; yet there is no work extant in which there is a good and complete collection of such as relate to all the different departments of applied chemistry. It is proposed that the publication of a work, to be entitled ‘Chemical formulæ, and constants, for use in the Laboratory,’ be undertaken by the Society; and should this proposition be

favourably received by the Members, and a prospect afforded of the means of obtaining the required matter, the Council will be prepared to carry it into effect\*.

“The first of the Society’s publications, the volume of Chemical Reports and Memoirs, edited by Professor Graham, being out of print, those who now join the Society, and desire to obtain the whole of Gmelin’s Chemistry, are supplied with the first volume on payment of half the subscription for 1848. In anticipation of a continued demand, by new members of the Society, for all the volumes of Gmelin’s standard work, a larger number was printed than was immediately required, and copies still remain on hand.

“The Council trust that the interest evinced in the objects of the Association has been justified by the results of its operations, and that the exertions made for extending the limits of the Society, will not be relaxed until it has reached the point originally contemplated, and which is now so nearly approached.”

\* The Council will be glad to receive communications on this subject, addressed to the Secretary, from members who may be able to afford assistance by supplying or suggesting matter for the proposed work.

TREASURER'S STATEMENT OF THE RECEIPTS AND EXPENDITURE OF THE CAVENTISH SOCIETY,  
from the 1st of March, 1850, to the 27th of February, 1851.

| RECEIPTS.                  |                   | EXPENDITURE.                        |                   |
|----------------------------|-------------------|-------------------------------------|-------------------|
|                            | £ s. d.           |                                     | £ s. d.           |
| Balance from previous year | .. .. 278 18 6    | Stationery, Postage, and Petty cash | .. .. 15 4 3      |
| 94 Subscriptions for 1848  | .. .. 85 11 6     | Advertisements.. .. .               | .. .. 5 9 0       |
| 160 Ditto                  | .. .. 168 0 0     | Insurance .. .. .                   | .. .. 2 6 6       |
| 684 Ditto                  | .. .. 718 4 0     | Collector's Commission              | .. .. 12 11 3     |
| 95 Ditto                   | .. .. 99 15 0     | Secretary .. .. .                   | .. .. 75 0 0      |
| 1 Ditto                    | .. .. 1 1 0       | Editorial expenses                  | .. .. 195 15 0    |
|                            |                   | Paper.. .. .                        | .. .. 145 16 7    |
|                            | <u>£1351 10 0</u> | Printing .. .. .                    | .. .. 395 2 0     |
|                            |                   | Engraver .. .. .                    | .. .. 2 11 0      |
|                            |                   | Binding and wrapping                | .. .. 94 10 6     |
|                            |                   |                                     | <u>944 6 1</u>    |
|                            |                   | Balance in hand                     | .. .. 407 3 11    |
|                            |                   |                                     | <u>£1351 10 0</u> |

5

We have examined the above statement, and find it correct.

R. PORRETT.  
R. H. SEMPLE

Feb. 28, 1851.



## Honorary Local Secretaries.

- Aberdeen*—Dr. R. Rattray.  
*Abergavenny*—Robert Falkener, Esq.  
*Bath*—J. P. Tylee, Esq.  
*Beccles*—W. E. Crowfoot, Esq.  
*Bedford*—W. Blower, Esq.  
*Belfast*—Dr. J. F. Hodges.  
*Birmingham*—Dr. John Percy, F.R.S.  
*Bodmin*—D. F. Tyerman, Esq.  
*Bolton*—H. H. Watson, Esq.  
*Brighton*—F. Busse, Esq.  
*Bristol*—Wm. Herapath, Esq.  
*Cambridge*—W. H. Miller, Esq.,  
     M.A., F.R.S.  
*Carlisle*—Dr. H. Lonsdale.  
*Cheltenham*—Nathaniel Smith, Esq.  
*Chester*—R. D. Grindley, Esq.  
*Cirencester*—John Wilson, Esq.  
*Clifton*—G. F. Schacht, Esq.  
*Colchester*—Dr. Williams.  
*Cork*—Thomas Jennings, Esq.  
*Coventry*—Francis Wyley, Esq.  
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*Dublin*—Dr. J. Apjohn.  
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Mar. 17, 1886.

ON THE  
CHROMATE OF CHROMIUM,  
AND ANALOGOUS CHROMATES.

BY  
FRANK H. STORER  
AND  
CHARLES W. ELIOT.

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From the Proceedings of the American Academy of Arts and Sciences, Vol. V.

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Four hundred and ninety-third meeting.

March 12, 1861.

MONTHLY MEETING.

The PRESIDENT in the chair.

Professor C. W. Eliot read the following paper: —

*On the Chromate of Chromium, and analogous Chromates, with a New View of the Constitution of the Black Oxide of Manganese.* By FRANK H. STORER and CHARLES W. ELIOT.

I. CHROMATE OF CHROMIUM ( $\text{Cr}_2\text{O}_3$   $\text{CrO}_3$ ).

1. When a solution of monochromate of potash is mixed with a solution of any ter-salt of chromic oxide, the mixture immediately becomes brownish red, a bright brown precipitate subsides, and when this precipitate has been completely deposited, the liquid separated by filtration will present the clear yellowish-red color of bichromate of potash. The chrome salt may be chrome alum, or sulphate of chromic oxide, or hydrated sesquichloride of chromium, and, if a sufficient excess of chromate of potash be added to the solution, the precipitate and the filtrate will present the appearances described. This filtrate may be evaporated and crystallized; the resulting crystals will be a mixture of bichromate of potash and of sulphate of potash or chloride of potassium, as the case may be: often crystals of monochromate of potash will also present themselves. We prepared the precipitate for analysis by mixing a solution of chrome alum with an excess of monochromate of potash. The brown precipitate was washed with cold water: the color of the wash-water, at first bright yellow, became gradually paler, but never colorless. Twice in the course of the seven days during which the washing was continued, the precipitate was transferred from the filter to a mortar, stirred up with water, and thrown upon a fresh filter. This pro-

cess deepened the yellow color of the wash-water in each case. It being quite evident that the color of the wash-water was due to chromic acid abstracted from the precipitate, the washing was stopped on the eighth day, the precipitate was dried at  $50^{\circ}$  to  $55^{\circ}$ , and analyzed as follows. A portion was dissolved in very dilute nitric acid by the aid of a gentle heat; the color of the solution was a red brown. Ammonia, added in very slight excess to this solution, kept at the boiling point for half an hour, produced a brownish-green precipitate of chromic oxide, which looked the browner because it floated in a bright yellow liquid. This precipitate was filtered off and thoroughly washed with hot water; it then presented the common appearance of chromic oxide, and was ignited and weighed in the usual manner. The filtrate from this precipitate and the wash-waters were concentrated by evaporation, and acidified with acetic acid. Acetate of lead then precipitated the whole of the chromic acid contained in the yellow liquid, and after the subsidence of the precipitate the supernatant liquid was perfectly colorless. The chromate of lead was washed and weighed on a tared filter as usual. The result of the analysis was

|                         |   |       |                      |
|-------------------------|---|-------|----------------------|
| $\text{CrO}_3$          | = | 16.27 | per cent             |
| $\text{Cr}_2\text{O}_3$ | = | 46.43 | " "                  |
| Water                   | = | 37.30 | " " (by difference). |

This examination showed, first, that the washed precipitate was a compound of chromic acid and chromic oxide; secondly, that it was more basic than any supposable definite compound of these two bodies; thirdly, that the prolonged washing removed chromic acid from the substance originally precipitated. To study the effect of the washing upon the precipitate, we prepared a considerable quantity of the brown precipitate by mixing a concentrated solution of pure chrome alum with a large excess of a concentrated solution of monochromate of potash. The precipitate as first collected upon the filter of course retained a considerable quantity of the bichromate of potash, chromate of potash, and sulphate of potash which existed in the filtrate. The precipitate was quickly rinsed with cold water until these mechanically adhering salts seemed to have been removed. During this short washing the substance underwent no change in color or in any other external property. A portion was now removed from the filter, air-dried on a brick, and submitted to analysis (analysis  $\alpha$ ). The rest of the precipitate was washed for six hours with cold water; another portion



was then taken from the filter, air-dried, and analyzed (analysis *b*). Through the remainder (perhaps two teaspoonfuls) of the precipitate five litres of water were passed; another portion was then dried at  $100^{\circ}$  and analyzed (analysis *c*). When dried at  $100^{\circ}$  the precipitate is much less readily soluble in dilute nitric acid, than when not so heated, but the difficulty is easily overcome. The method of analysis was that described above.

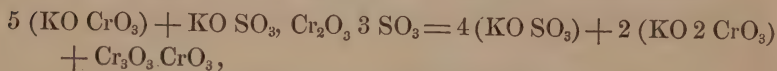
*Analyses.*

|                         | <i>a.</i>       | <i>b.</i>       | <i>c.</i>       |
|-------------------------|-----------------|-----------------|-----------------|
| $\text{Cr}_2\text{O}_3$ | 39.69 per cent. | 45.26 per cent. | 65.17 per cent. |
| $\text{CrO}_3$          | 22.42 " "       | 15.12 " "       | 8.87 " "        |
| HO (by diff.)           | 37.89 " "       | 39.62 " "       | 25.96 " "       |

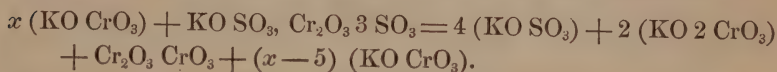
A comparison of these three determinations teaches that the abstraction of chromic acid by washing with cold water stops at no definite point, and probably has no limit except the complete change of the original precipitate into chromic oxide. The composition of the substance *a* must be a close approximation to the composition of the original precipitate, for the slight rinsing which was intended merely to remove the chromates belonging to the filtrate could hardly have abstracted much of its combined chromic acid. In the chromate of chromium whose formula would be  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ , the ratio of the chromic oxide to the chromic acid would be that of 3 : 2; and we find that the ratio of the chromic oxide to the chromic acid in analysis *a* is but little larger than that of 3 : 2. The substance *a* is probably therefore a chromate of chromium of the formula  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ , from which a little of the chromic acid has been removed by washing.

Assuming for the present that the precipitate produced by the reaction of chrome alum on monochromate of potash is in truth this chromate of chromium, let us inquire into the nature of the reaction between these two salts by which this precipitate could be formed, and bichromate of potash left in the filtrate. Concentrated solutions of pure chrome alum and of pure monochromate of potash were prepared of known strengths, in order to determine the amount of either solution required to produce a precipitate in the other. A single drop of chrome alum solution produces an immediate and permanent precipitate in the chromate solution; but if the process be reversed and the solution of monochromate of potash be dropped into the alum solution, no permanent precipitate is formed till an apparently large excess of chromate

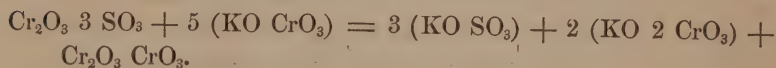
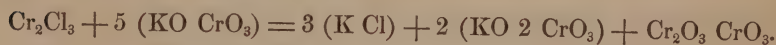
of potash has been added. By accurate quantitative experiments we have proved that five equivalents of chromate of potash must be added to one equivalent of chrome alum to effect precipitation. If a less quantity be added, any precipitate which may form will at once redissolve when the mixture is made complete by agitation.\* The reaction between the two salts may therefore be expressed by the formula,



and if to one equivalent of chrome alum more than five equivalents of chromate of potash be added, the excess above five remains inactive.



If any other normal salt of chromic oxide be used, a similar formula will express the reaction; thus:—



With the exact proportions of chrome alum and chromate of potash which are by the formula necessary for the precipitation of chromate of chromium we prepared a quantity of the precipitate for a second series of analyses in corroboration of analyses *a*, *b*, and *c*. The precipitate thrown upon a filter was very slightly rinsed with cold water, a portion of it was taken off, pressed between folds of filter-paper under heavy weights, and air-dried for analysis (analysis *d*); the rest of the precipitate was washed for six hours till no trace of the filtrate could possibly be supposed to be retained by the precipitate, when another portion was taken out for analysis, pressed, and air-dried (analysis *e*); lastly five litres of water were passed through the remaining precipitate, which was then dried at 100° and submitted to analysis (analy-

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\* In this connection we would call attention to the inaccuracy of the statement made by Berzelius in his *Traité de Chimie*, (Paris, 1846, Vol. II. 307), to the effect that a compound whose formula is  $\text{Cr}_2\text{O}_3 \cdot 3 \text{CrO}_3$  is precipitated, when a few drops of the solution of monochromate of potash are added to the solution of a neutral chrome salt. No permanent precipitate whatever is produced under these circumstances, as any one may satisfy himself by repeating the simple experiment described above.

sis *f*). The process of analysis was the same described above, and the results were as follows :—

*Analyses.*

|                         | <i>d.</i>       | <i>e.</i>       | <i>f.</i>       |
|-------------------------|-----------------|-----------------|-----------------|
| $\text{Cr}_2\text{O}_3$ | 38.85 per cent. | 44.01 per cent. | 59.83 per cent. |
| $\text{CrO}_3$          | 25.91 “ “       | 19.88 “ “       | 13.43 “ “       |
| HO (by diff.)           | 35.24 “ “       | 36.11 “ “       | 26.74 “ “       |

This set of analyses corroborates the first series in every respect, and the ratio of the chromic oxide to the chromic acid of the substance *d* is almost precisely the ratio 3 : 2 of the chromic oxide to the chromic acid in the chromate of chromium  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ . We again see that there is no definite limit to the removal of chromic acid by prolonged washing, and that the substance may be readily made more basic than any imaginable definite compound of chromic oxide and chromic acid would be.

In these analyses the precipitates had been somewhat washed before any analysis was made; it remained to analyze the substance precipitated with so much of the adhering filtrate as could not be removed by pressure between folds of filter-paper without washing. One precipitate (analysis *g*) was prepared by mixing a solution of one equivalent of chrome alum with eight equivalents of chromate of potash in solution, and a second by mixing a solution of one equivalent of chrome alum with sixteen equivalents of chromate of potash in solution (analysis *h*). In both cases the solutions used were concentrated and the precipitates air-dried. The method of analysis which we had heretofore employed was open to one objection,—a trace of chromic oxide was liable to be dissolved in the excess of ammonia, to be again separated when the filtrate and wash-waters from the chromic oxide precipitate were concentrated by evaporation, and the process would obviously be altogether inadmissible in any case where the sulphates of the mother-liquor had not been removed by washing before submitting the precipitate to analysis, since sulphate of lead would be formed and vitiate the determination of the chromic acid. We therefore resorted to Rose's method of separating chromic oxide from chromic acid, by means of the nitrate of the suboxide of mercury.\* The solution of the substance to be analyzed in dilute nitric acid was nearly neutralized with carbonate of potash, and when the carbonic acid had been allowed sufficient time to escape, nitrate of the suboxide of mercury was added,

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\* Handbuch der Analytischen Chemie, (Braunschweig, 1851,) II. 379.



the precipitate filtered off, washed, strongly ignited, and the chromic acid calculated from the pure chromic oxide which remained. To the filtrate from this first precipitate ammonia in excess was added, and the washed precipitate, strongly ignited, was the chromic oxide contained in the original substance.

*Analyses.*

|                         | <i>g.</i>       | <i>h.</i>       |
|-------------------------|-----------------|-----------------|
| $\text{Cr}_2\text{O}_3$ | 33.06 per cent. | 33.54 per cent. |
| $\text{CrO}_3$          | 32.03 " "       | 30.53 " "       |
| HO (by difference)      | 34.91 " "       | 35.93 " "       |

It is quite evident from these analyses that the precipitate caused by mixing chromate of potash with a neutral chrome salt cannot contain more than one equivalent of chromic acid in combination with its chromic oxide, since in the above determinations the chromic acid is nearer one equivalent than two with reference to the chromic oxide found, in spite of the fact that the considerable amount of chromic acid which, combined with potash, has adhered mechanically to the precipitate, is thrown down by the nitrate of the suboxide of mercury, together with the chromic acid which was originally united to the chromic oxide. But the fact that the substance under examination cannot be purified by washing without altering its constitution, renders it impossible to ascertain the exact composition of the body by the methods of analysis heretofore used, or by any similar methods; for this purpose the process used by Vogel\* in analyzing this same substance, obtained by him from a different source and misnamed  $\text{CrO}_2$ , is admirably adapted. The precipitate examined by this method was not washed at all, but was simply dried by pressure between folds of filter-paper and exposure to the air. A weighed portion was placed in the bulb of a reduction-tube, with which a weighed chloride of calcium tube was connected; a current of dry air was then drawn through the apparatus, and the reduction-tube was cautiously heated till all the water of the precipitate had been absorbed by the weighed chloride of calcium tube, the heat finally rising to dull redness. The salts with which the precipitate under examination was contaminated were sulphate of potash, bichromate of potash, and a little chromate of potash, and since the solutions from which the precipitate was prepared were concentrated, it was to be

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\* Jour. pr. Ch., LXXVII. 484 (1859).

expected that a considerable quantity of these salts would adhere to the precipitate; but since all these salts are fixed at a low red heat, they were not altered by the heat to which the precipitate was exposed. The rest of the precipitate must have lost by the ignition all its water and all the oxygen over and above that necessary to the constitution of chromic oxide. By subtracting the weight of the water collected from the total loss by ignition, the weight of the oxygen expelled is obtained. The ignited residue was then washed out of the bulb of the reduction-tube, digested in hot water, thrown upon a filter and washed with hot water till only pure chromic oxide remained; lastly, this oxide was ignited and weighed. By subtracting the weight of the chromic oxide from the weight of the whole ignited residue, the weight of the soluble salts which adhered mechanically to the precipitate was obtained. The following are the figures of an analysis by this method:—

|                                                     |               |
|-----------------------------------------------------|---------------|
| Weight of reduction-tube + precipitate              | 10.3848 gram. |
| “ “ “                                               | 9.6136 “      |
| “ “ precipitate                                     | 0.7712 “      |
| Weight of reduction-tube after ignition             | 10.2673 “     |
| Loss by ignition                                    | 0.1175 “      |
| Weight of residue                                   | 0.6537 “      |
| Weight of CaCl tube after ignition                  | 17.4196 “     |
| “ “ “ “ before “                                    | 17.3204 “     |
| “ “ water                                           | 0.0992 “      |
| “ “ oxygen = .1175 — .0992 =                        | 0.0183 “      |
| Weight of crucible + Cr <sub>2</sub> O <sub>3</sub> | 13.1275 “     |
| “ “ “ + filter ash                                  | 12.9601 “     |
| “ “ Cr <sub>2</sub> O <sub>3</sub>                  | 0.1674 “      |
| “ “ soluble salts = .6537 — .1674 =                 | 0.4863 “      |

In the compound whose formula is Cr<sub>2</sub>O<sub>3</sub> CrO<sub>3</sub>, the ratio of the number of atoms of oxygen to the number of atoms of chromium is that of 2 : 1. By adding another equivalent of oxygen to the chromic oxide found, we shall make the ratio of the atoms of oxygen to the atoms of chromium that of the compound Cr<sub>2</sub>O<sub>3</sub> CrO<sub>3</sub>. Hence the proportion.

$$\begin{array}{rclcl}
 (\text{Equiv. Cr}_2\text{O}_3) & & (\text{Equiv. O}) = (\text{Cr}_2\text{O}_3 \text{ found}) & & (1 \text{ equiv. O}) \\
 76.48 & : & 8 & = 0.1674 & : & x = 0.0175
 \end{array}$$

If the original precipitate was the compound whose formula is  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ , the loss of oxygen by ignition would have been 0.0175 gram.; the actual loss was 0.0183 gram., being within 0.0008 gram. of the theoretical amount. A loss of eight tenths of a milligramme in the water determination would of course account for this very small excess of oxygen.

A second analysis by this method of a precipitate containing a smaller proportion of soluble salts corroborated the first determination in every respect, and left no doubt that the true composition of the precipitate produced in the aqueous solution of a neutral salt of chromic oxide by the solution of chromate of potash is represented by the formula  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ .

2. Schweitzer\* observed that, when nitric oxide is passed through a moderately dilute solution of bichromate of potash, a brown precipitate separates after some time, especially if the liquid be slightly warmed. He did not analyze the substance, but remarks that it presents all the appearance of the brown oxide of chromium (so called). We prepared this compound by passing a stream of nitric oxide through a very dilute solution of bichromate of potash (a strong solution will not give the reaction so readily, if, indeed, at all) for three hours; in a few minutes the liquid became dark-colored and ceased to be transparent, but after standing twenty-four hours, during four of which it had been gently heated, there was still no apparent deposit; it was again warmed, and after sixteen hours more a slimy red-brown deposit was found at the bottom of the vessel. During forty-eight hours longer this deposit was allowed to accumulate, when the supernatant liquid was decanted and the precipitate thrown upon a filter. The decanted fluid continued to deposit very slowly this red-brown matter for days and weeks; indeed, in this, and several similar experiments, we have found no limit of time to the continuous, though very gradual, accumulation of this deposit. The slimy precipitate which had been filtered off was washed with hot water for twelve hours, the water at first coming through of a dark-red color, but growing gradually paler till it retained only a feeble yellow. The washing was continued for a week with cold water, and more than nine litres of water passed through the small precipitate. Whenever the color of the wash-water became so

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\* Jour. Pr. Ch., XXXIX. 269 (1846).



pale as to be hardly perceptible except with a considerable thickness of liquid, it was only necessary to transfer the precipitate to a mortar, rub it with water and throw it upon a fresh filter, in order greatly to intensify the yellow color of the filtrate. Believing that the chromic acid which colored the wash-water was derived from the decomposition of the precipitate, we stopped the washing on the eighth day, dried the precipitate at  $50^{\circ}$ – $55^{\circ}$ , and analyzed it by the first method described above. The color of the solution of the substance in dilute nitric acid was red-brown, and of the precipitate produced by ammonia, dirty green, which washing changed to the usual color of chromic oxide. The result of the analysis was,—

|                         |                   |
|-------------------------|-------------------|
| $\text{Cr}_2\text{O}_3$ | = 53.31 per cent. |
| $\text{CrO}_3$          | = 18.64 “ “       |
| HO (by difference)      | = 28.05 “ “       |

In regard to the ratio of the chromic oxide to the chromic acid, this result is very much like that of the first analysis given above (page 193), and leads to the same conclusions, viz. that the original precipitate is a compound of chromic oxide and chromic acid, from which prolonged washing abstracts chromic acid to an indefinite extent. We next prepared a new precipitate by passing nitric oxide through a dilute solution of bichromate of potash, and, without washing it at all, pressed it between folds of filter-paper, dried it by exposure to the air, and analyzed it by Rose's method, above described, with the following result:—

|                         |                   |
|-------------------------|-------------------|
| $\text{Cr}_2\text{O}_3$ | = 28.55 per cent. |
| $\text{CrO}_3$          | = 29.33 “ “       |
| HO (by difference)      | = 42.12 “ “       |

The object of this analysis was to prove that, even when the precipitate was contaminated with the chromates of the filtrate, the proportion of the chromic acid to the chromic oxide fell far below that which would exist in a compound containing two equivalents of chromic acid to one of chromic oxide, thus making it probable that the true formula of the precipitate is  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ .

To determine the exact proportions of chromic oxide and chromic acid in the original substance evidently requires a different process of analysis, and the third method of analysis described above is applicable to this purpose, with this advantage over the case to which we first

applied it, that the precipitate separates from such a dilute solution as to carry but a small proportion of soluble salts into the wholly unwashed deposit. The following are the figures of such an analysis of the precipitate pressed between folds of filter-paper without washing, and air-dried.

|                                                     |              |
|-----------------------------------------------------|--------------|
| Weight of the reduction-tube + precipitate          | 9.1856 gram. |
| “ “ “                                               | 8.5520 “     |
| “ “ precipitate                                     | 0.6336 “     |
| “ “ reduction-tube after ignition                   | 8.9342 “     |
| Loss by ignition                                    | 0.2514 “     |
| Weight of residue                                   | 0.3822 “     |
| Weight of CaCl tube after ignition                  | 17.6352 “    |
| “ “ “ before “                                      | 17.4210 “    |
| “ “ water                                           | 0.2142 “     |
| “ “ oxygen = .2514 — .2142                          | .0372 “      |
| Weight of crucible + Cr <sub>2</sub> O <sub>3</sub> | 35.0227 “    |
| “ “ “ + filter ash                                  | 34.7345 “    |
| “ “ Cr <sub>2</sub> O <sub>3</sub>                  | .2882 “      |
| “ “ soluble salts = .3822 — .2882 =                 | .0940 “      |

(Equiv. Cr<sub>2</sub>O<sub>3</sub>) : (Equiv. O) = (Cr<sub>2</sub>O<sub>3</sub> found) : (1 equiv. O).

The proportion  $76.48 : 8 = .2882 : x = .0302$  gives the theoretical amount of oxygen necessary to bring the chromic oxide found up to the composition expressed by the formula Cr<sub>2</sub>O<sub>3</sub> CrO<sub>3</sub> at 0.0302 gram.; the oxygen actually found was 0.0372 gram., being seven milligrammes in excess of the theoretical amount. When it is remembered that the unavoidable loss in the water determination, however small, tends to increase the amount of oxygen found, and that the loss in the chromic oxide determination tends to decrease the theoretical amount of oxygen, a discrepancy of only seven milligrammes will be considered allowable. A second analysis of the same precipitate by the same method gave even a nearer result, viz. :—

|                                                                                                                                      |              |
|--------------------------------------------------------------------------------------------------------------------------------------|--------------|
| Oxygen required to raise the Cr <sub>2</sub> O <sub>3</sub> found to the composition Cr <sub>2</sub> O <sub>3</sub> CrO <sub>3</sub> | 0.0235 gram. |
| Oxygen actually found                                                                                                                | 0.0264 “     |

These two analyses, in connection with the preceding determinations by the other methods, seem to us to prove conclusively that the precipitate produced by passing nitric oxide through a solution of bichromate

of potash is a chromate of chromic oxide, having the formula  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ . Schweitzer expressed his conception of the reaction by the formula



we shall write it, in accordance with the results of our analyses,



3. The same partial reduction of the chromic acid in bichromate of potash, which in the reaction just described is effected by nitric oxide, may be accomplished by alcohol with the aid of light. The precipitate so produced has been analyzed by Vogel,\* who assigns to it the composition which would be expressed by the formula  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ , though, for reasons hereafter to be considered, he seems to prefer the formula  $\text{CrO}_2$ . The precipitate thus obtained by alcohol† is identical in color and texture with that produced by nitric oxide, or by the double reaction between a neutral salt of chromic oxide and monochromate of potash. It is unnecessary in this connection to refer to the well-known reduction of aqueous chromic acid by sulphurous acid, by certain organic acids, by alcohol, and by paper; light and heat facilitate the reduction, and the brown chromate of chromic oxide is often produced when the reduction is but partial.‡

4. Again, the chromate of chromic oxide may be obtained by the oxidation of the hydrate of chromic oxide. When pure hydrated chromic oxide is treated with chlorine water, the oxide is converted into the brown chromate of chromic oxide, provided that the quantity of chlorine water be not sufficient to effect the solution of the chromate of chromic oxide formed in the chlorhydric acid which results from the reaction. Of course, the chromate of chromic oxide cannot be pre-

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\* Jour. pr. Ch., LXXVII. 482, (1859,) and Dingler's Polyt. J., CLIII. 391.

† We desire to correct a serious misprint in Vogel's note, as given in the *Journal für praktische Chemie* (LXXVII. 482), and thence transferred into Kopp & Will's *Jahresbericht für 1859*, p. 171. In the second line of the Article, "Ammoniak" should be "Alkohol." We trust this correction may save others the trouble we took before it occurred to us that the error was a typographical one, in endeavoring to verify or account for the marvellous statement that bichromate of potash was reduced by ammonia. The word is correctly printed in the abridgment of the same article given in Dingler's *Journal*, CLIII. 391.

‡ Gmelin's *Handbook* (Cavendish Soc. Ed.), IV. 119.



pared for analysis in this way, because a mixture of substances is the result to be expected from the incomplete reaction. Again, the partial oxidation of hydrated chromic oxide may be effected by exposing it for a long time to a temperature above  $200^{\circ}$ , but below redness, with free access of air.\*

The most precise statement on this subject has been made by Krüger, † whose main purpose was to prove that the glowing of ignited chromic oxide was due to the sudden escape of oxygen absorbed at a lower temperature, but who incidentally maintains that this absorption of oxygen gives rise to a definite oxide of chromium whose formula is  $\text{CrO}_2$ . We think to be able to show, first, that no definite compound whatever is formed during this imperfect oxidation; secondly, that the substance which really results from the prolonged heating contains chromic acid, and is an indeterminate approximation to the body whose formula is  $\text{Cr}_2\text{O}_3$   $\text{CrO}_3$ . It is obviously impossible to expose all parts of a substance in powder, like the hydrated chromic oxide, to the uniform action of the same quantity of air at the same temperature for the same time, and the limits of temperature between which the desired absorption of oxygen will take place most readily are not very clearly defined. Under these circumstances we should expect to obtain, not a definite compound, but a mixture, and the figures of Krüger's own analysis fully confirm this expectation. Krüger found 63.70 per cent of chromium and 36.30 per cent of oxygen in the body which he analyzed; the supposed oxide of chromium,  $\text{CrO}_2$ , would contain 62.12 per cent of chromium, giving a discrepancy of 1.58 per cent between the chromium of Krüger's substance and the chromium of the imaginary  $\text{CrO}_2$ . This does not seem an inadmissible error, till we

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\* The partial conversion of chromic oxide into chromic acid by gentle roasting seems to have been applied in the arts years ago. Cooley, in his *Cyclopædia of Practical Receipts*, (London, 1845, p. 263,) describes Charles Watt's process of preparing chromic acid from the oxide of chromium precipitated by lime from the residual liquor of the process of bleaching with chromic acid. The precipitate was heated evenly in a thin layer on a flat iron plate, with frequent stirring, till the mass assumed a yellow color. If too much heat was employed, the product of this operation was easily decomposed, assuming a green color. This process was apparently a true conversion of chromic oxide into chromic acid by roasting, and should not be confounded with the method of preparing chromate of lime described by Jacquelin (Ann. de Ch. et de Phys., [3.] XXI. 478), in which a mixture of lime and chrome-iron ore was heated to redness in a reverberatory furnace.

† Jour. pr. Ch., XXXII. 383, (1844,) and Pogg. Ann., LXI. pp. 219, 406.

observe that the whole difference between the chromium in chromic oxide (68.62 per cent) with which Krüger began, and the chromium in the supposed higher oxide  $\text{CrO}_2$  (62.12 per cent), is only 6.50 per cent, and that his error of 1.58 per cent in the amount of chromium is therefore nearly twenty-five per cent of the whole difference between the bodies  $\text{Cr}_2\text{O}_3$  and  $\text{CrO}_2$ . With so fatal a discrepancy between the actual and the theoretical figures, it is of course impossible to maintain that a definite oxide is obtained by such an indefinite process. We pass to the second point, the existence of chromic acid in imperfectly oxidized chromic oxide. Krüger thought to disprove the presence of chromic acid by heating the substance with sulphuric acid and common salt; no chromate or chloride of chromium being visible, he inferred the absence of chromic acid. This test is at best but an unsatisfactory one when applied to a very insoluble substance containing only a small proportion of chromic acid, and there seems to be no reason for trusting to a coarse reaction in a difficult case when very delicate tests are at hand. By heating hydrated chromic oxide for five hours to a temperature varying between  $200^\circ$  and  $210^\circ$  we obtained a brownish black powder, which dissolved with great difficulty in dilute acids, communicating a dark yellow color to the liquid. Digested with water, the powder yielded a partial solution of a bright yellow color, and this solution gave a very marked reaction for perchromic acid with the solution of peroxide of hydrogen.\* When quickly boiled with an aqueous solution of chloride of ammonium, the filtered solution was bright yellow, and gave the reaction of perchromic acid with peroxide of hydrogen. Would it not be difficult to explain this effect of aqueous chloride of ammonium on the brown powder on the supposition that its real composition was represented by the formula  $\text{CrO}_2$ ? Krüger endeavored to strengthen his position with regard to the absence of chromic acid, by heating with common salt and sulphuric acid a precipitate prepared by mixing bichromate of potash, sulphate of chromic oxide, and ammonia, and finding as before no chromate or chloride of chromium; he used the precipitate in one experiment air-dried, in another, dried at  $110^\circ$ . This precipitate was probably a mixture of chromic oxide with the chromate of chromic oxide, and, unless the last ingredient was present in very small proportion, it should have readily produced chromate or chloride of chromium. From a portion of the pre-

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\* Storer, Proc. Amer. Acad., IV. 138; Jour. pr. Ch., LXXX. 44.

precipitate used in analysis *f*, we obtained without difficulty the red chromate of chloride of chromium by heating it with chloride of sodium and strong sulphuric acid. We shall have occasion to cite below a similar experiment upon an anhydrous mixture of chromic oxide and chromic acid, obtained by gently igniting the nitrate of chromic oxide, in which the chromate of the chloride of chromium was very readily obtained. Relying on the yellow color imparted by the substance under examination to water and to chloride of ammonium, and on the ready exhibition of perchromic acid by means of peroxide of hydrogen, and explaining Krüger's failure to obtain chlorochromic acid by the fact that only a very small amount of chromic acid proportionally exists in the mixture, we conclude that, by long heating in the air, a part of the chromic oxide is converted into chromic acid, which instantly combines with other chromic oxide, and that the end of this process, seldom if ever attained, is the conversion of the whole mass into the chromate of chromic oxide,  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ .

5. Many chemists, among whom may be mentioned Vauquelin, Berzelius, Döbereiner, and Thomson, have tried the experiment of gently igniting the nitrate of chromic oxide, or, what amounts to the same thing, of evaporating to dryness nitric acid in contact with metallic chromium or hydrated chromic oxide, and moderately heating the residue. Some, like Berzelius,\* have thought that they obtained in this way a definite oxide of chromium, intermediate between chromic oxide and chromic acid, and answering to the formula  $\text{CrO}_2$ ; others, like Vauquelin,† have imagined that they obtained chromic acid by repeated evaporation of nitric acid with chromium, or have believed, with Thomson‡ and Gordon,§ that a great part of the green oxide was converted into chromic acid; while others still have maintained, with Döbereiner,|| that the chromate of chromic oxide was formed by the decomposition of the nitrate.

In order to a clear knowledge of the effect of evaporating nitric acid with chromic oxide, it is necessary in the first place to answer qualita-

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\* Thomson's *Ann. Phil.*, III. 104, (1814,) and Schweigger's *J. für Ch. u. Phys.*, XXII. 56.

† *Ann. de Chim.*, XXV. 201 (1798).

‡ *Phil. Trans.*, 1827, Part I. p. 206.

§ Rapport par MM. Berthollet et Vauquelin, *Ann. de Ch.*, LIII. 224.

|| Schweigger's *Jour. für Ch. u. Phys.*, XXII. 482 (1818).



tively the question, Is chromic acid formed during the process? A mixture of nitric acid and hydrated chromic oxide was gently evaporated, first on a water-bath, then upon a sand-bath, and before the free nitric acid was completely driven off, a portion of the moist mass was treated with a solution of caustic potash; it partially dissolved with a yellow color, and the solution gave the distinct blue of perchromic acid with peroxide of hydrogen. The rest of the evaporated residue was heated till it looked like a perfectly dry powder, but still retained the smell of nitric acid. In this condition a portion was treated with water, in which it slowly and partially dissolved, yielding a brownish yellow solution, which readily gave the blue of perchromic acid. A half of the remaining residue from the original evaporation was strongly heated in a porcelain dish on a sand-bath, and then digested with water during four hours; the solution so obtained was decidedly yellow, and gave easily the blue of perchromic acid. The other half of the residue was heated on platinum foil, till the platinum was of a dull red color in a darkened room, and was then soaked in water for thirty-six hours; the supernatant liquid was of a pale yellow color, and gave a faint blue with peroxide of hydrogen. The same substance treated with caustic potash gave a yellow solution.

With this qualitative evidence of the formation of an abundance of chromic acid at a moderate temperature, which is not wholly destroyed even at incipient redness, we proceeded to the quantitative determination of the amount of chromic acid formed at the different stages of the process. A quantity of pure hydrated chromic oxide was treated in a porcelain dish with an excess of pure nitric acid, and evaporated on a water-bath nearly to dryness; those parts of the substance which dried completely were moistened with nitric acid and again dried. The nitric acid could not be completely driven off on the water-bath; though the larger part of the mass seemed dry, yet portions of it were still moist when the process was stopped, and it was far from being homogeneous. The brownish black substance imparted a strong yellow tinge to water, and dissolved with difficulty in dilute nitric acid, giving a brownish yellow solution. A portion of it, analyzed by Rose's method, gave

$$\text{Cr}_2\text{O}_3 = 64.85 \text{ per cent.}$$

$$\text{CrO}_3 = 31.51 \quad "$$

$$\text{NO}_5 \text{ and HO} = 3.64 \quad " \quad (\text{by difference}).$$

It was now necessary to prepare for analysis from the evaporated residue a series of homogeneous substances, each of which had been exposed

to a little higher temperature than the preceding one, in order to exhibit the effect of different temperatures in the production of chromic acid. A portion (No. 1) of the evaporated residue was heated on a porcelain dish at a low temperature, with constant stirring, to complete dryness; a second portion (No. 2) was first thoroughly dried at the same temperature to which No. 1 had been exposed, and was then somewhat more strongly, but still very gently, heated for a few moments, during which nitrous fumes escaped in abundance; in this manner each substance was dried at the highest temperature to which the preceding one had been exposed, and was then subjected to a little stronger heat during five or ten minutes; the last substance (No. 5) was heated as hot as was possible, while avoiding incipient redness. The chromic acid of each substance was determined by precipitating it with nitrate of the suboxide of mercury; the chromic oxide was also determined in two or three cases, but only to control the analyses. All five substances were soaked in water for five hours; pure nitric acid was then added in very small quantity, and, at the end of forty-four hours more, solution had been effected in each case. The color of the dry powder was brownish black, that of the solutions brownish yellow. The percentage of chromic acid in each substance was as follows:—

|        | $\text{CrO}_3$ . |
|--------|------------------|
| No. 1, | 25.18 per cent.  |
| No. 2, | 26.09   “        |
| No. 3, | 48.52   “        |
| No. 4, | 55.49   “        |
| No. 5, | 60.39   “        |

It therefore appears that a variable amount of chromic oxide may be converted into chromic acid by evaporation with nitric acid, and that the quantity so changed increases with the increase of temperature till incipient redness is reached. If this mixture of chromic oxide, chromic acid, and nitric acid be exposed to a red heat, the nitric acid and the absorbed oxygen are driven off together, and nothing remains but insoluble chromic oxide. It is sufficiently clear from these results, that no definite compound can be formed during this evaporation of nitric acid in contact with chromic oxide; the result is simply an indeterminate mixture of chromic oxide and chromic acid. It may be remarked, in passing, that this mixture closely resembles in every external property the brownish black powder obtained by gently heating chromic oxide in

contact with the air, a substance which, as we have seen, is also an indeterminate mixture of chromic oxide and chromic acid, containing, however, very much less chromic acid than the mixture just examined. Substance No. 5 of the preceding series, although anhydrous, yields chlorochromic acid with salt and sulphuric acid with the greatest facility, another indication that the true explanation of Krüger's not obtaining chlorochromic acid from his heated chromic oxide is to be found in the fact that it contains too small an amount of chromic acid to be exhibited by that somewhat coarse reaction.

6. Many distinguished chemists have observed the reactions and studied several of the substances which we have here described, and no treatment of the subject can be complete which does not embrace an abstract of their labors. We shall therefore relate as concisely as possible the history of the substance which has been variously called brown oxide of chromium, or chromate of chromic oxide, and review the discussion as to its composition which has heretofore been brought to no satisfactory conclusion.

Vauquelin,\* the discoverer of chromium, obtained what he thought to be a brownish-red oxide of chromium by several methods, the details of which it is unnecessary to describe; it will be enough to observe, that neither of his methods gave him a definite compound; they all gave rise to indeterminate mixtures of the bodies now known as chromic oxide and chromic acid. He proved that nitric acid, whether cold or boiling, cannot oxidize chromic oxide, but that the calcination of the nitrate of chromic oxide produced a substance whose aqueous solution was red; ammonia precipitated from this solution the green oxide, and the separated filtrate was yellow. His experiments led Vauquelin to the conclusion, that there are two kinds of oxide of chromium, which differ only in the quantity of oxygen they contain.

Two errors, into which the reader of Vauquelin's papers might easily fall, demand notice. It might be inferred from some of his statements that the chromate of ammonia was a body readily decomposed by simple boiling with separation of the so-called brown oxide of chromium. We have found the chromate of ammonia to be a body possessing much greater stability than has been usually attributed to it; its aqueous solution will resist, without change, prolonged boiling,

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\* Ann. de Ch., LXX. pp. 85, 86 (1809).



concentration, and exposure for weeks to the direct rays of the sun. It is true that repeated evaporation to dryness may partially decompose it, and it is of course destroyed by ignition.

Again, Vauquelin asserts that ammonia will precipitate the brown oxide of chromium from an aqueous solution of chromic acid through which sulphurous acid has been passed, and this assertion seems to be confirmed by some statements, made without quoted authority in Gmelin's Handbook (Cavendish Soc. Ed., IV. 114), concerning salts of the brown oxide of chromium obtained by dissolving this hydrated oxide in acids, from which solutions it may be again precipitated by ammonia. This is an important point in determining the real existence of such an oxide of chromium, and we have therefore made it the subject of careful experiment. We have dissolved in dilute chlorhydric and dilute nitric acids such precipitates as analysis had shown to have very nearly the composition which is expressed by the formula  $\text{CrO}_2$  (as, for instance, the precipitate of analysis *d*, and of the analysis on page 201), and have added to the solutions ammonia of every strength, from the strongest to the weakest, and have so obtained one invariable result, viz. a precipitate of common green chromic oxide, and a filtrate made yellow by chromate of ammonia. It is true that the fresh precipitate has a dirty or brownish look, caused by its impregnation with the yellow liquid in which it floats; and this is the most probable explanation of the opinion held by some previous observers, that this precipitate was something more than ordinary chromic oxide.

The chief authority upon which the existence of salts of the brown oxide of chromium is asserted, seems to be that of Brandenburg,\* who obtained solutions of substances which his own experiments, rightly interpreted, prove to have been mixtures of chromic acid and salts of chromic oxide, but which he thought were salts of an imaginary higher oxide of chromium. There is no such thing as a salt of the brown oxide of chromium, for the reason that there is no such base.

It was the opinion of Döbereiner† that the substance produced by the calcination of the nitrate of chromic oxide was a chromate of chromic oxide and not an oxide of chromium, and he referred to the same formula the substances formed by the reduction of chromic

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\* Schweigger, Jour. für Ch. u. Phys., XIII. 287 - 289 and 299 - 304.

† Ibid., XXII. 482 (1818).

acid by paper, and by the digestion of chromic oxide with chromic acid.

Thomson\* prepared a brown precipitate, which he called brown oxide of chromium, by passing a stream of sulphurous acid through a solution of chromate or bichromate of potash. We have found, as did Berthier,† that no precipitate whatever is produced by passing sulphurous acid through bichromate of potash; but this is a point of no importance in this connection. Thomson washed the precipitate which he had obtained for two months, and noticed the steady abstraction of chromic acid from the precipitate. He finally analyzed the washed oxide (as he called it) and made it to be a very basic chromate corresponding to the formula  $(\text{Cr}_2\text{O}_3)_6 \text{CrO}_3$ . His opinion of the effect produced by the ignition of the nitrate of chromic oxide we have already cited. Under the head of chromate of chromium he remarks that, when chromic oxide is dissolved in chromic acid and the solution evaporated, there remains a substance quite similar in appearance to the brown oxide of chromium. Again, he observed the precipitate produced by mixing chromate of potash with sesquichloride of chromium, and says of it that it is evidently composed of chromic acid and the green oxide of chromium. Guided by the analogy of chromium and iron, he prepared a chromate of iron by mixing chromate of potash with sesquichloride of iron; an analysis of the edulcorated brown precipitate led him to the formula  $(\text{Fe}_2\text{O}_3)_5 \text{CrO}_3$ , and in the filtrate and wash-water he thought he found another less basic chromate, corresponding to the formula  $(\text{Fe}_2\text{O}_3)_5 (\text{CrO}_3)_{2.5}$ . On the whole, Thomson seems to have believed in the existence of a brown oxide of chromium, intermediate between chromic oxide and chromic acid; but every one of his experiments and analyses points directly to the conclusion, that the supposed oxide is in reality a chromate of chromic oxide, or rather in most cases an indeterminate mixture of chromic oxide and chromic acid.

We come now to the researches of Maus,‡ contemporaneous with those of Thomson, but much more conclusive upon the disputed point as to the existence of a distinct oxide of chromium answering to the formula  $\text{CrO}_2$ . Maus mixed an aqueous solution of sesquichloride of chromium with chromate of potash, and digested the washed precipitate

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\* Phil. Trans., 1827, Part I. p. 186.

† Ann. der Ch. u. Pharm., XLVI. 185 (1843).

‡ Pogg. Ann., IX. 127 (1827).

with acetate of lead, thereby obtaining a green solution of acetate of chromic oxide and a yellow precipitate of chromate of lead; he treated the same substance with arsenic acid, and obtained the insoluble arseniate of chromic oxide and chromic acid in solution. By washing the original precipitate for three weeks he claims to have removed all the chromic acid, and says that nothing but chromic oxide remained. By mixing sesquichloride of iron with chromate of potash he prepared a similar chromate of iron, from which all the chromic acid could be removed by washing in the same way. He believed that the calcination of the nitrate of chromic oxide produced a chromate of chromium, but containing always nitric acid, because a heat sufficient to drive off all the nitric acid also converted the chromate of chromium into chromic oxide. Maus did not analyze quantitatively any of these precipitates, probably because he was embarrassed by the impurities from which he could not free the precipitates without altering their composition; but his qualitative results are amply sufficient to prove that they all contained chromic acid as part of their original constitution. Maus did analyze two substances prepared by digesting chromic oxide and ferric oxide in chromic acid; the results of these analyses were, —

| 1.                                        | 2.                                        |
|-------------------------------------------|-------------------------------------------|
| $\text{Cr}_2\text{O}_3 = 27.79$ per cent. | $\text{Fe}_2\text{O}_3 = 25.06$ per cent. |
| $\text{CrO}_3 = 72.21$ “                  | $\text{CrO}_3 = 74.94$ “                  |

And he assigned to them the formulæ  $\text{Cr}_2\text{O}_3 \cdot 2 \text{CrO}_3$  and  $\text{Fe}_2\text{O}_3 \cdot 2 \text{CrO}_3$  respectively. These formulæ are incorrect; the figures of the first analysis would give about four equivalents of acid to one of the oxide, and those of the second analysis would give more than four equivalents of chromic acid to one of ferric oxide. Both substances were unquestionably indeterminate mixtures. Dumas, recounting the experiments of Maus, says, “These results would be decisive, but they are contested by Berzelius.”\* It is therefore necessary to review the opinions of Berzelius on this subject.

In 1814 Berzelius, writing an essay on the “Cause of Chemical Proportions,”† mentions the new oxide of chromium, prepared by Vauquelin, intermediate between the green oxide and chromic acid. Berzelius

\* *Traité de Chimie Appliquée*, (Liège, 1848,) VII. 319.

† Thomson's *Ann. Phil.*, III. 104, (1814,) and Schweigger's *Jour. für Ch. u. Phys.*, XXII. 56.



prepared this oxide, as he supposed, by igniting the nitrate of chromic oxide, observed the external properties of the substance, but did not analyze it, and made use of it only as an aid in establishing the contents of oxygen in chromic acid. In this essay he states the formulæ of the oxides of chromium as  $\text{CrO}_3$ ,  $\text{CrO}_4$ , and  $\text{CrO}_6$ , the last being the acid. In a subsequent paper,\* in speaking of the oxides of chromium, he lays special stress upon the close relation between manganese and chromium, and on the isomorphism of the sesquioxides of aluminum, chromium, manganese, and iron. He now writes the formula of chromic oxide as  $\text{Cr}_2\text{O}_3$ , and in all probability the peroxide of manganese ( $\text{MnO}_2$ ) was in his mind an argument for the oxide  $\text{CrO}_2$ , though he does not mention it in the paper referred to. Finally, in 1829, Berzelius† rejects the conclusions arrived at by Maus, and gives the following reasons for his continued belief in the existence of the oxide  $\text{CrO}_2$ . The first reason urged is the analogy between the sulphur acids and the oxides of chromium; this comparison is based merely on the isomorphism of chromic and sulphuric acids. In the light of the better knowledge both of the sulphur acids and of the oxides of chromium which thirty years have given us, and with the clearer notions of chemical classification which now prevail, we can find in the existence of sulphurous acid no argument for the existence of an oxide of chromium containing two atoms of oxygen. Secondly, Berzelius gives his own idea of the reaction consequent upon mixing chromate of potash with sesquichloride of chromium, which he thinks is not correctly described by Maus; according to Berzelius, the decomposition between these two salts does not take place at once, but the mixed solution first becomes dark yellow, soon changes to brown, a brown precipitate separates, and the liquid remains brown; hence he infers the formation of two compounds of chromium and oxygen, one soluble and represented by the formula  $\text{Cr}_2\text{O}_5$ , the other the insoluble  $\text{CrO}_2$ . We have accurately described in the first sentences of this paper the phenomena presented on mixing a solution of sesquichloride of chromium with a solution of chromate of potash, and have subsequently given the formula which represents the reaction. There is no reason to suppose that any such compound as  $\text{Cr}_2\text{O}_5$  remains in solution; when the brown precipitate first formed has completely subsided, the color of the filtrate is that of bichromate of potash. Lastly, Berzelius accounts for the fact that the

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\* Pogg. Ann., VII. 415 (1826).

† In his Jahresbericht, VIII. 123.

supposed oxide yields to analysis chromic acid and chromic oxide by imagining that the original oxide is decomposed by contact with water into chromic acid and chromic oxide, as hyposulphurous acid is decomposed by water into sulphurous acid and sulphur, or as nitrous acid is resolved by water above  $0^{\circ}$  into nitric oxide and a solution of nitric acid ( $3 \text{NO}_3 + \text{Aq} = 2 \text{NO}_2 + \text{NO}_5 + \text{Aq}$ ). This might perhaps be a possible supposition, if the brown substance in question were prepared by methods in which water had no part; but when we see it precipitated from dilute solutions of monochromate of potash and a neutral chrome salt, or subsiding in the course of days from a very dilute solution of bichromate of potash, we are forced to the conclusion, that the substance is from the first composed of the chromic acid and chromic oxide which analysis shows it to contain. In short, we have all the evidence, analytical and synthetical, that this brown precipitate is a chromate of chromic oxide, which we have of the real constitution of sulphate of potash.

The compound is well worthy the attention of those chemists who deny that formulæ ever express the actual constitution of bodies; it seems questionable whether any formula for the chromate of chromium can readily be written on the unitary theory which will express its properties and reactions as well as the dualistic formula. When at this distance we look back at the feebleness of the theoretical arguments which Berzelius opposed to the facts of Maus, Thomson, Döbereiner, and others, we marvel at the weight of a name whose authority outweighed the accumulated evidence of several trustworthy observers, and prevented the truth from prevailing thirty-four years ago. Berzelius himself became much less confident in after years of the truth of his earlier views; in his *Traité de Chimie*\* he calls the precipitate formed by mixing a neutral chrome salt with chromate of potash, chromate of chromic oxide, and in a subsequent paragraph merely says that it is very possible that this compound is the oxide of chromium,  $\text{CrO}_2$ .

An observation made by Rammelsberg† added something to our knowledge of the precipitate formed by mixing a solution of chrome alum with a solution of chromate of potash. He made a determination of the water contained in the washed precipitate, and weighed the chromic oxide obtained by igniting it; the oxygen which was expelled by ignition was determined by loss. The analysis led to the formula  $(\text{Cr}_2\text{O}_3)_3 (\text{CrO}_3)_2 + 9 \text{HO}$ , showing that the washing of the precipitate

\* II. 307 (Paris, 1846).

† Pogg. Ann., LXVIII. 274 (1846).

had been sufficient to make it somewhat basic. The point specially noticeable in Rammelsberg's statement is his assertion that the precipitate was washed till it imparted no color to cold water. This is not credible, for the testimony of all other chemists is unanimous upon the point, that there is no limit to the removal of chromic acid by washing from this precipitate. We have often prepared much more basic precipitates, and have never yet seen colorless wash-water from the most basic of them. The color may become so pale as not to be very noticeable in small vessels.

The discussion which we have traced left the subject in such doubt and obscurity, that most writers of text-books have given both views of the substance in question, some leaning to one theory of its composition, some to the other. In our endeavor to settle the question, we shall next bring to bear upon the subject the arguments to be drawn from analogy.

## II. ANALOGOUS CHROMATES.

The metals with which chromium is allied are aluminum, iron, and manganese, and the existence of chromates of the sesquioxides of these metals with properties analogous to those which we have described as belonging to the chromate of chromic oxide, will be additional evidence that this substance is rightly so called.

1. *Chromate of Alumina.* Maus\* observed, but did not analyze, the chromate of alumina which is precipitated when chromate of potash is added to a solution of alumina in chromic acid; he speaks of it as "consisting of chromic acid with much alumina." When the precipitate was thoroughly washed, pure hydrate of alumina remained on the filter and acid chromate of alumina passed into the filtrate. Fairrie† also describes a chromate of alumina prepared by mixing alum solution with the solution of chromate of potash, and his analysis led to the exact formula  $\text{Al}_2\text{O}_3 \cdot \text{CrO}_3$ ; he states, however, that the precipitate was thoroughly washed, which in connection with the result of his analysis is quite incomprehensible; for Maus observed, and our own experiments fully confirm his observation, that all the chromic acid may be readily washed out of this compound.

The yellow precipitate which appears when chromate of potash is dropped into a solution of alum, is constantly re-dissolved until the proportion of chromate of potash added amounts to five equivalents to each

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\* Pogg. Ann., XI. 82 (1827).

† Jour. Chem. Soc., IV. 301 (1852).



one of alum; the precipitate then becomes permanent; it is light yellow in color, and has a gelatinous appearance which suggests an excess of alumina. The reaction is evidently the same as that above given for the precipitation of chromate of chromic oxide.  $5 (\text{KO CrO}_3) + \text{Al}_2\text{O}_3 + 3 \text{SO}_3, \text{KO SO}_3 = 4 (\text{KO SO}_3) + 2 (\text{KO } 2 \text{CrO}_3) + \text{Al}_2\text{O}_3 \text{CrO}_3$ . The precipitate was drained, pressed between folds of filter-paper under heavy weights, and air-dried. The filtrate, when evaporated and crystallized, gave crystals of bichromate of potash, and of sulphate of potash mixed with the slight excess of chromate of potash. The presence of soluble salts in the pressed precipitate, and its decomposition by washing, determined us to the third method of analysis above described (p. 197). Omitting the subsidiary weighings, we give the essential figures of our first analysis of this substance.

|                                                                          |              |
|--------------------------------------------------------------------------|--------------|
| Weight of the precipitate analyzed                                       | 0.5997 gram. |
| “ “ water found                                                          | 0.1948 “     |
| “ “ oxygen “                                                             | 0.0197 “     |
| “ “ soluble salts found                                                  | 0.1969 “     |
| “ “ mixed precipitate of $\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3$ | 0.1883 “     |

It will be remembered that the water and the precipitate of chromic oxide and alumina are actually weighed, the oxygen being determined by subtracting the water found from the total loss by ignition, and the soluble salts by subtracting the weight of the precipitate of chromic oxide and alumina from the weight of the whole residue after ignition. The amount of chromate of alumina corresponding to the oxygen lost by ignition may be calculated as follows:—ignition drives off half of the oxygen originally combined with the chromium; hence

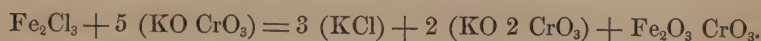
|                                           |   |        |
|-------------------------------------------|---|--------|
| Oxygen in the chromic acid of precipitate | = | 0.0394 |
| Chromic acid corresponding to this oxygen | = | 0.0825 |
| Chromate of alumina “ “ chromic acid      | = | 0.1666 |

This calculation rests entirely upon the single determination of the oxygen, and an inspection of the steps of the process will show that any error in the amount of oxygen, or rather in the water determination on which the weight of oxygen depends, is multiplied by eight and a fraction in the calculated amount of chromate of alumina. A considerable discrepancy is therefore to be expected between the amount of chromate of alumina so calculated, and the amount actually found in the

analysis, the sum of the oxygen and of the mixed precipitate of chromic oxide and alumina. That sum is in this analysis 0.208 gram.; subtracting the calculated amount 0.1666 gram., we find a discrepancy of 0.0414 gram. By subtracting 0.005 gram. only from the weight of the water determined, this error would be corrected, and the precipitate would coincide exactly with the formula  $\text{Al}_2\text{O}_3 \cdot \text{CrO}_3$ , or, as the figures stand, its composition is very nearly that represented by the formula  $(\text{Al}_2\text{O}_3)_3 (\text{CrO}_3)_2$ . Of course a method of analysis involving such a multiplication of an error, however small, is objectionable, but we were at a loss to devise a better. A second analysis gave a similar result; the discrepancy between the calculated and the actual numbers was four milligrammes larger than in the first analysis, and the figures of the analysis gave a chromate of alumina a little more basic than that represented by the formula  $(\text{Al}_2\text{O}_3)_3 (\text{CrO}_3)_2$ . We attach very little importance to any such formula. The fact seems to be that the normal composition of the chromate of alumina precipitated by the double decomposition of alum and chromate of potash is represented by the formula  $\text{Al}_2\text{O}_3 \cdot \text{CrO}_3$ , but that the compound is a feeble one, and parts readily with some of its chromic acid to the water of the solutions from which it is precipitated; hence the basic character of the precipitate analyzed. How Fairrie obtained a thoroughly washed chromate of alumina having the formula  $\text{Al}_2\text{O}_3 \cdot \text{CrO}_3$  is a mystery upon which our experiments have thrown no light.

2. *Chromate of Iron.* We have already cited the observations of Thomson concerning this chromate, which he found after washing to be very basic, and also the statement of Maus concerning the acid chromate of iron with four equivalents of chromic acid, obtained by digesting hydrated sesquioxide of iron in aqueous chromic acid. It remained for us to analyze, as exactly as the circumstances permit, the unwashed chromate of iron which is precipitated when chromate of potash is mixed with perchloride of iron. The method of analysis was the same as that used for chromate of alumina, with the disadvantage that the error in the amount of oxygen found is multiplied by ten instead of by eight in calculating the chromate of iron, because the atomic weight of the sesquioxide of iron is larger than that of alumina. The stability of the chromate of iron is greater, however, than that of the chromate of alumina, and the results of the analyses are very much nearer to the formula  $\text{Fe}_2\text{O}_3 \cdot \text{CrO}_3$ , than those of chromate of alumina to the formula  $\text{Al}_2\text{O}_3 \cdot \text{CrO}_3$ . The formula for the reaction whereby the brown chro-

mate of iron is precipitated, is the same as those already given for chromate of chromic oxide and chromate of alumina, viz. :—



Until the requisite amount of chromate of potash had been added to the perchloride of iron, the precipitate re-dissolved; when it became permanent, it was drained, pressed, and air-dried for analysis.

### *Analysis 1.*

|                                                                            |              |
|----------------------------------------------------------------------------|--------------|
| Weight of the precipitate analyzed,                                        | 0.6626 gram. |
| “ “ water found,                                                           | 0.0966 “     |
| “ “ oxygen “                                                               | 0.0395 “     |
| “ “ soluble salts found,                                                   | 0.2288 “     |
| “ “ mixed precipitate of $\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ , | 0.2977 “     |

From these data may be obtained by the necessary proportions,—

|                                                                                               |        |
|-----------------------------------------------------------------------------------------------|--------|
| Oxygen in the chromic acid of precipitate,                                                    | 0.0790 |
| Chromic acid corresponding to this oxygen,                                                    | 0.1654 |
| Chromate of iron corresponding to this chromic acid,                                          | 0.4287 |
| Chromate of iron found = $\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{O}$ weighed = | 0.3943 |
| Excess of the calculated chromate of iron over the found =                                    | 0.0344 |

This error would be perfectly corrected by a loss of three milligrammes in the water determination, or as the figures stand without any correction they would lead to the conclusion that the precipitate was a chromate of iron of the formula  $\text{Fe}_2\text{O}_3 \text{ CrO}_3$ , but containing a very small excess of chromic acid.

### *Analysis 2.*

|                                                                            |        |
|----------------------------------------------------------------------------|--------|
| Weight of the precipitate analyzed,                                        | 0.6590 |
| “ “ water found,                                                           | 0.0990 |
| “ “ oxygen “                                                               | 0.0360 |
| “ “ soluble salts found,                                                   | 0.2254 |
| “ “ mixed precipitate of $\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ , | 0.2986 |

From these data may be obtained by the necessary proportions,—

|                                                      |        |
|------------------------------------------------------|--------|
| Oxygen in the chromic acid of precipitate,           | 0.0720 |
| Chromic acid corresponding to this oxygen,           | 0.1197 |
| Chromate of iron corresponding to this chromic acid, | 0.3597 |



Chromate of iron found =  $\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{O}$  weighed = 0.3346  
 Excess of the calculated chromate of iron over the found = 0.0251

This error would be corrected by a supposed loss of little more than two milligrammes in the water determination. This second analysis, therefore, confirms the view that the normal composition of this chromate of iron is represented by the formula  $\text{Fe}_2\text{O}_3 \text{ CrO}_3$ .

It is unnecessary to call attention to the great similarity of the properties of the chromates of chromic oxide, ferric oxide, and alumina; their normal composition is represented by the formula  $\text{R}_2\text{O}_3 \text{ CrO}_3$ , but they are such feeble compounds as seldom to be found of the exact constitution which the formula indicates.\* Of the three, the chromate of chromic oxide is the most stable, and we have been able to prepare it with the exact theoretical composition, from which it so easily varies. It should be observed, that a variation in the composition of these chromates, amounting to even ten per cent of their chromic acid, does not affect in the least their external properties, and it is by no means impossible that they are examples of that variation in the law of definite proportions which has been ably discussed by Professor J. P. Cooke in the Memoirs of this Academy; † but unfortunately, as must often be the case, the limits of error of our methods of analysis are wider than those of the supposed variation, and moreover, on this border-land between the kingdoms of Chemical and of Mechanical Force, there must always be doubt and difference of opinion concerning the cause to which a proved effect is to be ascribed.

3. *Chromate of Manganese.* The existence of this chromate has been so clearly demonstrated by previous observers that we have thought it unnecessary to add any experiments of our own. On mixing a solution of sulphate of the protoxide of manganese with a solution of chromate of potash, a chocolate-colored precipitate subsides after some time, to which Warington ‡ assigned the formula  $(\text{MnO})_2 \text{ CrO}_3 \cdot 2 \text{ HO}$ . Bensch § also analyzed a similar precipitate, for which he gives the same formula. In Warington's analysis the amount of protoxide of manganese is larger than the compound which his formula rep-

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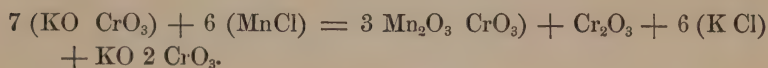
\* The monochromate of glucina mentioned by Gmelin (Handbook, IV. 155, Cavendish Soc. Ed.) evidently belongs to this class.

† New Series, V. pp. 348, 352 (1854).

‡ Phil. Mag., [3.] XXI. 380 (1842).

§ Pogg. Ann., LV. 98 (1842).

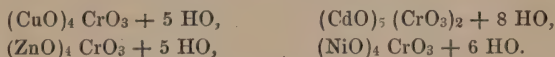
resents would contain, and it is, moreover, questionable if the protoxide of manganese could exist in contact with chromic acid. The subsequent observations of Fairrie\* explain these difficulties. He mixed the solutions of chloride of manganese and chromate of potash, and so obtained a precipitate whose composition by analysis was  $3 (\text{Mn}_2\text{O}_3 \text{ CrO}_3) + \text{Cr}_2\text{O}_3 + 6 \text{HO}$ . Fairrie's criticism on the analyses of Warrington and Bensch, that they overlooked the chromic oxide formed by the reaction, is no doubt just. He also remarks, that the precipitate appeared to be formed by the action of seven equivalents of chromate of potash on six equivalents of chloride of manganese, but offers no explanation of the reaction. The decomposition is explained by the formula,



Six equivalents of the protoxide of manganese are oxidized into three equivalents of sesquioxide of manganese, at the expense of the three atoms of oxygen which two equivalents of chromic acid give up in changing into one equivalent of chromic oxide; probably the chromic oxide so formed enters into combination with the chromate of manganese, rendering it basic. Chloride of potassium and bichromate of potash remain in the filtrate.†

\* Jour. Chem. Soc., IV. 300 (1852).

† We do not wish to leave the subject of the metallic chromates without noticing the remarkable analyses published by Malaguti and Sarzeau (Ann. de Ch. et de Phys., [3.] IX. 431, 1843) of the chromates of copper, zinc, cadmium, and nickel. The figures of these analyses correspond exactly with the following singular formulæ:—



All these precipitates were washed with boiling water till no color came from them, and it is clear that these chromates, like those which we have studied, may be deprived of the greater part of their chromic acid, if not the whole, by prolonged washing; hence the basic character of the substances analyzed. The marvel is, that the analyses corresponded so exactly with such peculiar formulæ; it is hardly conceivable that the publication of many analyses of each of these substances should not show the existence of a series of compounds, which conform to no definite formulæ.

### III. THE BLACK OXIDE OF MANGANESE ( $3 \text{ MnO}_2 = \text{Mn}_2\text{O}_3 \text{ MnO}_3$ ).

Another question now suggests itself, — Would analogy lead us to suppose that there was an oxide of chromium containing two atoms of oxygen? Comparing chromium, as before, with the allied metals, aluminum, iron, and manganese, we meet with no such oxide of aluminum, and we have Fremy's \* direct statement that he could find no oxide of the formula  $\text{FeO}_2$ . Manganese, however, forms a compound with oxygen, stable, insoluble, and natural, which has heretofore always been spoken of as an oxide of manganese and been represented by the formula  $\text{MnO}_2$ . Is not the existence of this compound a strong argument for the oxide  $\text{CrO}_2$ ? We propose to adduce the evidence which makes it most probable that this so-called peroxide of manganese is in reality a compound, sometimes definite but oftener indefinite, of manganic acid and manganic oxide, and that its normal composition is to be represented by the formula  $\text{Mn}_2\text{O}_3 \text{ MnO}_3$ .

We shall not expect to resolve this substance into manganic oxide and manganic acid with the same facility with which we analyze the chromate of chromic oxide. This latter body is less stable than either chromic oxide or chromic acid, whereas manganic acid and oxide are both exceedingly unstable substances, obtained with difficulty but easily destroyed. On the other hand, there is no more stable compound of manganese than that called the peroxide. It is not therefore decomposed, as the chromate of chromium is, by boiling water, boiling caustic potash, or a boiling solution of chloride of ammonium. We prepared artificial peroxide of manganese by passing a stream of chlorine through water in which carbonate of protoxide of manganese was diffused, and washing the precipitate, first with dilute nitric acid and then with water. The artificial peroxide thus prepared resisted solutions of chloride of sodium and of caustic potash, even when heated with these liquids in closed tubes to a temperature of  $180^\circ$  by means of a wax bath.

But, notwithstanding the stability of this black oxide of manganese, it is not impossible to obtain from it manganic acid under circumstances which seem to preclude the possibility of any oxidation of the substance during the process by which the manganic acid is exhibited. Mitscherlich † observed and reported the formation of the green manganate of

\* Ann. de Ch. et de Phys., [3.] XII. 381.

† Abhandlungen der Akademie der Wiss. zu Berlin, 1831, p. 218. Ann. de Ch. et de Phys., [2.] XLIX. 114. Pogg. Ann., XXV. 287.



potash, when caustic potash is fused in a retort with peroxide of manganese *without access of air*. Upon such authority this statement must have great weight, although the omission of the details of the experiments renders it impossible to form any opinion of the sufficiency of the evidence upon which it rests. Fortunately the results of Mitscherlich find full confirmation in the recent experiments of Bekétóff.\* This observer has shown that, when a mixture of caustic potash and black oxide of manganese is heated, in a closed tube filled with oxygen, to a temperature of  $180^{\circ}$ , an abundance of the green manganate of potash is formed *without the slightest absorption of oxygen*. Unless these experimental results can be disproved, it seems impossible to escape the conclusion that the substance called peroxide of manganese contains manganic acid, since it yields manganic acid while the ratio of its manganese to its oxygen remains unchanged.

In 1817 Chevillot and Edwards† published an account of some experiments in which they endeavored to prove that the presence of air or oxygen was absolutely necessary to the formation of chameleon from caustic potash and black oxide of manganese. To demonstrate this, they first heated the mixture of these two substances in a silver crucible, within a glass vessel which was filled with nitrogen, and found that no manganate of potash was produced. The amount of heat applied is not stated, but the nature of the apparatus indicates that a high temperature was used. Secondly, they heated the same mixture of caustic potash and black oxide of manganese in an atmosphere of oxygen, and measured the considerable quantity of oxygen absorbed during the formation of the manganate. These experiments seem at first sight absolutely to contradict those of Mitscherlich and Bekétóff; but it is easy to show that they have no such tendency, and that the conclusions which Chevillot and Edwards drew from them were entirely erroneous, though the experiments themselves were perfectly correct and faithfully reported. It is obvious that an absorption of oxygen is just as necessary in order to convert the substance, whose formula would be written  $\text{Mn}_2\text{O}_3 \cdot \text{MnO}_3$ , *completely* into manganic acid, as it is for the entire conversion of the so-called oxide  $\text{MnO}_2$  into the same acid. The same amount of oxygen must be absorbed in changing one gramme of the black oxide of manganese into manganic acid, however the rational formula of

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\* Bulletin de Soc. Chim. de Paris, Séance 13 Mai, 1859, I. 43.

† Ann. de Ch. et de Phys., [2.] IV. 290.

that substance may be written. To prove that oxygen is absorbed during the formation of manganate of potash from caustic potash and black oxide of manganese, is therefore not at all to the purpose; the only question is, Can *any* manganate be formed *without* absorption of oxygen? This question the experiments of Mitscherlich and Bekétoff answer in the affirmative. But if manganate of potash is formed from caustic potash and black oxide of manganese without any addition of oxygen, how is the fact of its non-formation in an atmosphere of nitrogen, as proved by Chevillot and Edwards, to be accounted for. We have repeated the experiments of Chevillot and Edwards with a somewhat different apparatus. A combustion-tube of small diameter was nearly filled with copper turnings, and beyond the copper a platinum boat containing a mixture of caustic potash and peroxide of manganese was inserted. The tube was then connected with an aspirator, and a slow current of air was drawn through the hot copper. When time enough had elapsed to secure the complete filling of the tube with nitrogen, the platinum boat was heated gradually up to dull redness without producing a trace of the green manganate. When the tube had cooled, the contents of the boat was a fused, brownish mass. Another experiment, however, showed conclusively that the non-appearance of the green manganate is accounted for by the fact that this manganate cannot exist in an atmosphere of nitrogen at such a temperature. We prepared some manganate of potash in a platinum boat by fusing a mixture of carbonate of potash and black oxide of manganese in the air, and then heated this boat with its contents in an atmosphere of nitrogen by means of the apparatus just described. At a temperature very much below a red heat every trace of the green manganate disappeared, and when the tube was cool the appearance of the contents of the boat was that of a fused, brownish mass, precisely like that described above in the former experiment. Repetitions of the experiments fully confirmed these results, which perhaps ought to have been anticipated, since it seems more than probable that nitrogen would be oxidized in contact with a hot manganate. Similar experiments with an atmosphere of carbonic acid led to the same negative results. It must be borne in mind that our present purpose is merely to show the fallacy of the inferences which Chevillot and Edwards drew from their experiments, which were made at an uncertain but high temperature. We by no means wish to assert that it is impossible to obtain the green manganate of potash from a mixture of caustic potash and black oxide of manga-

nese in an atmosphere of nitrogen, if the temperature be sufficiently low. On the contrary, we have made several experiments which tend to the conclusion that this is perfectly possible under certain conditions. A mixture of caustic potash and natural black oxide of manganese was placed in a glass tube, which was then filled with nitrogen and sealed. Thus hermetically closed, the tube was heated in a wax-bath to  $180^{\circ}$  for three hours; at the end of the experiment, we found that portions of the mass in the tube had been changed into green manganate of potash, though the greater part seemed to be unaltered. Again, a mixture of potash and the black oxide, artificially prepared, was gently heated in a combustion-tube in a current of nitrogen to a temperature barely high enough to fuse the mass, and the manganate of potash was formed, small in amount, but perfectly unmistakable. In repeating this last experiment, however, we failed quite as often as we succeeded, for it is difficult to heat the mixture hot enough to insure the formation of the manganate without also heating it hot enough to destroy it. Moreover, no experiments, intended to exhibit the formation of manganate of potash in nitrogen from potash and the black oxide, can be conclusive, so long as the experimenter is unable to answer any one who may please to allege that the nitrogen used contained a trace of oxygen. Unless some method of preparing the nitrogen is used which will enable the chemist to assert that the gas is free from oxygen and from all other impurities which might affect the reaction, such experiments will establish nothing. The only conclusive method of testing the question whether manganate of potash can be formed from the black oxide and potash alone, is that so well applied by Bekétoff, who proved that the manganate can be produced from these materials in an atmosphere of oxygen at a low temperature without the slightest absorption of that gas. His experiments were obviously performed with such care that we have thought it superfluous to repeat them.

We have been at such pains to review and explain the experiments of Chevillot and Edwards, in order to put the decomposition of the substance called peroxide of manganese into manganic oxide and manganic acid in its true light, as an uncontradicted fact, resting upon the highest authority. If we add to this decomposition of the black oxide of manganese by potash the other fact, that it is a perfectly neutral or indifferent body, possessing none of the properties either of an acid or of a base, we have evidence, not sufficient perhaps absolutely to prove that its true rational formula is  $\text{Mn}_2\text{O}_3 \cdot \text{MnO}_3$ , but quite enough to show



that the formula  $\text{MnO}_2$  is no argument for the formula  $\text{CrO}_2$ , in the face of the demonstration of the true character of the chromate of chromium heretofore given. On the contrary, the fact that the supposed brown oxide of chromium is in reality composed of chromic oxide and chromic acid, gives additional weight to the experimental evidence already accumulated, that the peroxide of manganese is a compound of manganic oxide and manganic acid. There is a striking similarity between the methods of preparing chromate of chromium and manganate of manganese, the more noticeable in view of the very different stabilities and solubilities of the oxides of these two metals. Thus the action of chlorine on chromic oxide gives rise to the formation of chromate of chromium, while its action on the carbonate of manganous oxide produces the manganate of manganese.\* Again, the gentle ignition of the nitrate of manganous oxide produces a mixture of manganous oxide with the higher oxides of manganese; this mixture contains so much manganate of manganese that the process has been patented as a method of obtaining a manganese oxide adapted to the preparation of chlorine.† This result corresponds precisely with the result of igniting the nitrate of chromic oxide. Again, the absorption of oxygen by heated chromic oxide exposed to the air, observed by Krüger, finds its exact parallel in the absorption of oxygen by manganous oxide under the same circumstances. A mixture of the higher oxides of manganese is so obtained, and this process of ignition has been long known in the arts as a means of "revivifying" black oxide of manganese, rendering it available for the preparation of chlorine a second time, or through an indefinite series of alternate reductions and oxidations.‡

\* Gmelin's Handbook of Chemistry, IV. 207, Cavendish Soc. Ed.

† Berthier, *Ann. de Chim. et de Phys.*, [2.] XX. 187. Gatty, *Eng. Patent Specifications*, 22 Aug. 1857, No. 2230, p. 3.

‡ Pfaff. *Schweigger's Jour. für Ch. u. Phys.*, LIII. 122, (1828).

Binks, C. *Eng. Patent Specifications*, 8 Feb. 1839, No. 7963, pp. 4, 8, and 9.

Ebelmen. *Ann. des Mines*, [3.] XVII. 517 (1840).

Walters, G. S. *Eng. Patent Specifications*, 24 Mar. 1843, No. 9676.

Balmain, W. H. " " " 31 Mar. 1855, No. 723, p. 4.

Dunlop. " " " 22 Nov. 1855, No. 2637, p. 3.

Barrow. " " " 26 Feb. 1856, No. 485, pp. 4, 9.

Elliot. " " " 13 Oct. 1856, No. 2392, p. 4.

Pattinson. " " " 21 Oct. 1856, No. 2475.

Gossage. " " " 8 Nov. 1856, No. 2630, p. 7.

Reissig. *Ann. der Ch. u. Pharm.*, CIII. 27 (1857).

In several of these specifications the removal of alumina and sesquioxide of iron

While it is much easier to obtain the manganate of manganese in a state of tolerable purity than it is to prepare the chromate of chromium, because of the greater insolubility of the first substance, it would nevertheless be very difficult, to say the least, to precipitate it by the method of double decomposition. We can readily mix chromate of potash and a normal salt of chromic oxide, and throw down the chromate of chromic oxide: till we can prepare a pure and neutral manganate of potash, the true composition of the manganate of manganic oxide cannot be illustrated in this way.

#### IV. OTHER CHROMATES OF CHROMIC OXIDE.

Under the head of "Bichromate of Chromic Oxide" the English Editor of Gmelin's Handbook of Chemistry\* has described two processes, neither of which has any connection with the name and formula at the head of the paragraph; the first is the description of a washed, and therefore basic, chromate of chromic oxide, prepared by Traube,† identical with the substance analyzed by Rammelsberg, as Traube himself remarks, and having the same formula by Traube's analysis, viz.  $(\text{Cr}_2\text{O}_3)_3 (\text{CrO}_3)_2$ ; the second is the description of the mode of precipitating the chromate of chromic oxide,  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ , from chrome alum by chromate of potash in the manner we have fully explained.

For the existence of what the translator of Gmelin's‡ Handbook calls the "Neutral Chromate of Chromic Oxide," with the formula  $\text{Cr}_2\text{O}_3 \cdot 3 \text{CrO}_3$ , there seems to be no sufficient evidence. Unverdorben, Berzelius, and Maus have proved beyond a question, what hardly required proof, that when heated above the melting point chromic acid is ultimately resolved into oxygen and chromic oxide. Traube§ has thought to show that by using a temperature but little above  $250^\circ$  a definite chromate can be obtained, corresponding to the formula  $\text{Cr}_2\text{O}_3 \cdot 3 \text{CrO}_3$ . By heating a quantity of chromic acid to this re-

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is described, preparatory to the roasting of the manganous salt or oxide. The more manganic acid formed by the roasting the better, — may not then the admixture of a certain amount of these bases be chemically advantageous? Very possibly there are mechanical advantages to be gained by their removal.

\* Handbook of Chemistry, IV. 115 (Cavendish Soc. Ed.).

† Ann. der Ch. u. Pharm., LXVI. 108 (1848).

‡ Handbook of Chemistry, IV. 116 (Cavendish Soc. Ed.).

§ Ann. der Ch. u. Pharm., LXVI. 106 (1848).

quired temperature he obtained a black mass which had taken the shape of the crucible; this he powdered and digested with water, with the expectation of dissolving that portion of the chromic acid which had not been affected by the heat; the wash-water after some days still remaining yellow, he concluded that the substance itself gradually dissolved, and proved this to his own satisfaction by analyzing two portions, one of which had been washed more than the other, with the same result, viz. 57.93 per cent of chromium and 42.07 of oxygen. These figures correspond to the formula  $\text{Cr}_2\text{O}_3 \cdot 3 \text{CrO}_3$ . Now chromic acid contains 52.23 per cent of chromium and chromic oxide 68.62 per cent, and in changing from the first into the second, under the influence of a moderate heat, the heated substance will at some moment contain 57.93 per cent of chromium; before that moment it would contain less, after that moment more. We were not so fortunate as to hit on the right time for stopping the experiment. We subjected a mass of chromic acid to a temperature a little above  $250^\circ$  for three hours, and obtained a brownish black substance, such as Traube has described, which, powdered and boiled with water, imparted a faint yellow color to the liquid. Analysis showed that it contained 54.12 per cent of chromium. It is quite clear that any substance prepared in such a way must be a mixture, and that the particular mixture analyzed by Traube has no claim to the name and formula of a definite compound.

Still another hypothetical chromate, called "Soluble Brown Chromic Oxide or Acid Chromate of Chromic Oxide," figures in Gmelin's Handbook (*loc. cit.*). Maus and many others have made a solution of hydrated chromic oxide in aqueous chromic acid, but Maus alone has analyzed the solution; we have already expressed our opinion that the liquid he analyzed was only an indeterminate mixture (p. 211). The observation and the conjecture of Berzelius, cited by Gmelin in this paragraph, we have already remarked upon; the precipitate which Berzelius speaks of is the chromate of the formula  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ .

To sum up the case, — there is not a particle of evidence of the existence of any chromate of chromium containing more than one equivalent of chromic acid. Such may be hereafter discovered, but it does not seem probable that they will be found to be insoluble compounds. Until the realities are made known to us, why cumber the science with names and formulæ, which fill no gaps, extend no analogies, bridge no difficulties, but are merely a perplexity and a hinderance? It has been too much the custom to call the chromate of the formula  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$



the *basic* chromate of chromium ; this proceeds on the assumption that there is some other salt better entitled to the name of normal or neutral chromate, as, for example, the imaginary chromate containing three equivalents of chromic acid. Until some such chromate is discovered, the word *basic* would be better omitted from the name of the only definitely determined chromate of chromium.



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CHEMICAL CONTRIBUTIONS

TO THE

July, Nov., and Sept. Nos.

OF

SILLIMAN'S JOURNAL.

BY

M. CAREY LEA.

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— neque nos agere hoc, patriai tempore iniquo
Possumus æquo animo.—*Lucr.*

ON THE PRODUCTION OF THE ETHYL BASES.

BY M. CAREY LEA,
PHILADELPHIA.

I MENTIONED in a former number of this Journal that while engaged in the examination of the action of ammonia on certain oxy-ethers, I had met with the experiments of Juncadella and De Clermont, and finding that the production of ethylamine by these reactions had been already indicated, I discontinued my investigations. Subsequently however having occasion to prepare a considerable quantity of ethylamine for other examinations, I determined to ascertain whether the action of nitrate of ethyl on ammonia could not be made use of as a convenient process. Juncadella had already proposed to mix nitrate of ethyl with three or four parts of alcohol, saturate the mixture with dry ammoniacal gas, and heat for two days to 212° in the water bath. This was a rather troublesome process, and a few experiments led me to the following very simple method, which I publish as having given me satisfactory results:

Nitrate of ethyl is mixed with an equal volume of strong alcohol. To this mixture is added a quantity of ordinary strong liquid ammonia equal in bulk to that of the mixture. The nitrate of ethyl is thereby precipitated but is nevertheless easily acted upon by the ammoniacal liquid. Three hours in the water bath at 212° is generally sufficient to complete the reaction. As the process goes on the nitrate of ethyl becomes brownish, gradually diminishes and finally disappears. The resulting solution does not contain salts of ammonia and ethylamine only, as has been stated, but *a large quantity of diethylamine and triethylamine.*

As the nitrate of ethyl can be prepared in large quantity with great facility by a modification of M. Millon's process, which will appear with some other papers in the following number of this Journal, I am inclined to think that this process will be found valuable for the preparation of the ethyl bases. It is necessary that the tubes should be strong, and not more than two-thirds full. Bottles hermetically sealed are not to be recommended unless extremely strong. In one experiment I operated with four eight ounce bottles all of which stood the test, but on

repeating the process three of the four exploded at once and the fourth subsequently.

The presence of alcohol is far from being essential. Nitrate of ethyl is readily decomposed at 212° by aqueous ammonia, and if the ammonia is in considerable excess, the decomposition is complete in three hours. If the excess is only slight the time required for decomposition is greatly increased. In one experiment where 29 parts of nitrate of ethyl were heated with 57 of liquid ammonia, the decomposition was not complete till at the end of 15 hours. The use of alcohol and the proportions above given are what was found to give the most satisfactory result.

Philadelphia, April 9, 1861.

ON THE EXACT SEPARATION OF THE ETHYL BASES.

BY M. CAREY LEA,
PHILADELPHIA.

It has been known for some time that when ammonia was acted upon by the hallogen ethers, the ethylamine produced was always accompanied by a variable quantity of the secondary and tertiary ethyl bases and the ammonium base, and I have shown that the same is the case with respect to the secondary and tertiary ethyl bases in the reactions of oxy-ethers. The ammonium base I have not looked for, but it is doubtless present also. The primary, secondary and tertiary bases resemble each other so closely in their properties that their separation is attended with great difficulty and has generally been effected by the different solubilities of their chloroplatinates.* I find however that it may be accomplished with great ease by means of picric acid. The picrates of the different bases exhibit the most opposite degrees of solubility, the picrate of triethylamine rivalling the picrate of potash in insolubility, while that of diethylamine is soluble to an almost unlimited extent in water, alcohol and ether, without being in the least deliquescent. Its affinity for ether is so great that its concentrated ethereal solution will remain exposed to the atmosphere for days in a syrupy condition, gradu-

* Dr. Hoffman has lately described an elegant mode of separation, differing however, entirely from that here proposed, viz. by means of oxalic ether.

ally crystallizing on the surface, and eventually all through, to a radiated mass. Between these two extremes the picrate of ethylamine occupies an intermediate position and the differences of solubility are so well marked as to render the separation perfectly easy in the manner to be indicated below.

1. Separation of the mixed bases from Ammonia.

This has been generally directed to be done by treating the mixed hydrochlorates either with absolute alcohol, or with a mixture of strong alcohol and ether, whereby the salammoniac is supposed to be left undissolved.

This process I have always found to the last degree unsatisfactory, and necessarily so; for if absolute alcohol be allowed to stand over salammoniac in powder for a time and then be evaporated in a watch glass, a certain quantity of salammoniac will be deposited and the same is true of a mixture of strong alcohol and ether. By operating on the ammonias in the form of sulphates a much more satisfactory result is obtained. For this purpose the mixture as poured out from the pressure tube is treated with a sufficient quantity of pure sulphuric acid to displace the nitric acid (or if bromid or iodid of ethyl have been employed, the bromhydric or iodhydric acid) and the solution is evaporated as far as possible at a temperature of about 250° F. The pasty mass is exhausted with strong alcohol, the alcoholic solution is evaporated as far as possible at the same temperature and the residue exhausted with a small quantity of absolute alcohol. Two exhaustions at least, are necessary even when absolute alcohol is used the first time. In this way a satisfactory result is obtained, which cannot be accomplished with the chlorhydrates.

2. Separation of the mixed bases from each other.

TRIETHYLAMINE.

After being completely freed from ammonia as above described, the mixed sulphates were distilled with caustic potash, in the usual way and the bases were saturated with crystallized picric acid. Sufficient heat was applied to redissolve the precipitate which formed toward the close of the saturation, and the hot (not too concentrated) solution allowed to crystallize. The first crop of crystals thus obtained were purified by several re-crystallizations, the chlorhydrate of the base was formed and from this the chlorplatinate which was obtained in large and beautiful crystals. The platinum salt was analyzed.

4858 gms. substance gave 1567 platinum,	Per cent.
This corresponds to	32.26
Chloroplatinate of triethylamine contains	32.23

The close correspondence of the result with the number given by theory indicates the perfect purity of the triethylamine. Its proportion is but inconsiderable compared with that of ethylamine and diethylamine, and it is chiefly contained in the first portion of the gaseous products which pass over in the distillation with caustic potash.

Picrate of triethylamine crystallizes in delicate yellow needles, which dissolve sparingly in cold water and alcohol, abundantly in hot. The decrease of solubility in an aqueous or alcoholic solution as it cools is very sudden, so that a hot solution deposits almost the whole of the salt as it begins to cool. Placed on platinum foil and gently heated, it melts, turns first red, then black, at the same time boiling up, takes fire, and leaves a residue of charcoal.

ETHYLAMINE.

After the least soluble salt had been removed in the manner just described, the mother water deposited another crop of crystals, which were purified by repeated recrystallization, the chlorhydrate of the base was formed, and its chlorplatinate was analyzed.

·4429 gms. substance gave ·1728 platinum.	Per cent.
This corresponds to	39·02
The chloroplatinate of ethylamine contains	39·29

Picrate of ethylamine presents great differences of appearance according to accidental circumstances. When first crystallizing out of the mixed solution it usually forms groups of short brown prisms adhering to the bottom of the basin. If these be recrystallized we obtain long yellow flattened prisms and laminae, extending in every direction through the liquid—few substances exhibit more beautiful crystallization. A dilute alcoholic solution often deposits flat prisms bevelled at the extremities, and sometimes hexagonal plates.

In solubility in water this substance approximates to the picrate of ammonia, to which, after it has been subjected to repeated recrystallizations, it bears considerable resemblance in appearance.

DIETHYLAMINE.

After the picrate of ethylamine has been for the most part removed, the mother waters exhibit a curious phenomenon which greatly simplifies the further purification of the diethylamine salt left in solution. When these mother waters have been a little reduced by spontaneous evaporation or by a gentle heat, the liquid spontaneously separates into two layers, a pale yellow lighter and a dark brown heavier. The evaporation is continued

until the heavier layer constitutes rather more than half of the whole, and then the two layers are separated either at once by a separating funnel, or ether may be added and thoroughly shaken up, when the brown layer dissolves in the ether and rises to the top. After separation it is allowed to crystallize and is once or twice recrystallized from a small quantity of ether by which it is obtained quite pure. A specimen was converted into chlorhydrate and then into chlorplatinate, and gave the following results on analysis:

·3884 gms. substance gave ·1377 platinum.	Per cent.
This corresponds to	35·45
Chloroplatinate of diethylamine should contain	35·45

It appears therefore that the salt obtained in the above described manner is perfectly pure.

Picrate of Diethylamine without being deliquescent is soluble to almost any extent in water, alcohol and ether. By spontaneous evaporation it crystallizes in a radiated mass. Sometimes at the bottom of the vessel beautiful transparent brown yellow crystals form, which belong to the monoclinic system. Combination observed $\infty P\infty$, $[\infty P\infty]$, $0P$, ∞P , $+P$, and a clinodiagonal doma.

The approximate proportions in which the different ethyl bases were produced by the reaction here made use of were perhaps ten per cent of triethylamine, thirty or forty of diethylamine and fifty or sixty of ethylamine.

The method here described gives with facility a very exact separation of these bases. The only precaution necessary to be observed, especially in operating on small quantities, is that the solution must not be too concentrated at the outset, otherwise the picrate of triethylamine will be mixed with picrate of ethylamine. But the delicate needles of the former are easily distinguished from the broader ones and prismatic crystals of the latter, and two or three recrystallizations suffice to separate them completely.

I feel assured that picric acid will be found to be a most valuable reagent in effecting separations of cognate organic bases. It may be doubted if there exists any other acid whose salts taken as a whole exhibit so marked a tendency to ready crystallization, and the great differences in the solubility of picrates of allied bases, adds as in the foregoing example, to the value of this acid in effecting separations between them.

Philadelphia, April 9, 1861.

CHEMICAL CONTRIBUTIONS,

BY M. CAREY LEA.

1. *On the Preparation of Nitrate and Nitrite of Ethyl.*

NITRATE OF ETHYL.

THE tendency of alcohol to decompose nitric acid is so great that while we have any number of processes for obtaining nitrite of ethyl, Millon's is the only one known for forming the nitrate. But Millon's process fails much oftener than it succeeds (such at least has been my experience) in consequence of the proportion of urea directed to be used being much too small.

Millon's process as quoted in Kolbe's *Organische Chemie*, directs to distill equal weights of alcohol and of colorless nitric acid sp. gr. 1.401. Not to operate upon larger quantities than 120 to 150 grammes, and to add a little urea, to the above quantity, at most ("höchstens") 2 grammes of urea.

Conducted as above, the operation succeeded with me but once out of four or five times. But by using a large quantity of urea, three or four times as much, or even more, success invariably follows, and there results a great saving of urea, because when the process fails, the materials, urea included, are entirely lost, whereas when conducted as just described, very little urea is consumed. It is only necessary to add fresh acid and alcohol, after the first proportion has been distilled to about one fifth, and the process may be repeated almost indefinitely, with the occasional addition of a little urea to keep up the proportion. The product in the second and subsequent operations is much larger than in the first.

Nor have I found it necessary to operate on the small quantities above mentioned, but have habitually used quantities

amounting to 400—500 grammes, and should not hesitate to employ still larger ones. It is however more convenient to use the above quantity, and replace the material as fast as exhausted.

The facility with which nitrate of ethyl can be obtained by the above process must, I think, give it a decided advantage over the iodid of ethyl for the preparation of the ethyl bases, in the manner which I described in the last number of this Journal. The lower equivalent of nitric acid as compared with iodine is a matter of considerable importance, one hundred parts of iodine are capable of holding in combination something less than 23 of ethyl, whereas one hundred parts of nitric acid combine with over 53 of ethyl; a material point as the iodine on the one hand and the nitric acid on the other are merely the vehicles for bringing about the ethyl-substitution. In operations in pressure tubes where space is valuable, this is an important consideration; in an economical point of view also, the advantage appears to be greatly on the side of the nitrate of ethyl.

NITRITE OF ETHYL.

The action of nitric acid on alcohol in the preparation of nitrite of ethyl may be conveniently moderated by protosulphate of iron, and the nitric acid reduced by that agent instead of at the expense of part of the alcohol. The proportions which I have used are, nitric acid sp. gr. 1.37, 90 cc., alcohol of 90 per cent, 150 cc., ferrous sulphate 45 grammes. The product is very large, the distillate on being shaken up with water yields more than half its bulk of nitrite of ethyl. The latter is not perfectly free from aldehyd, but more so than that obtained by some other processes. The action is perfectly quiet to the last, and the distillation may be carried on rapidly.

2. *On the Effects of Reducing Agents upon Nitrite of Ethyl.*

As ammonia under the influence of oxydizing agents is burned to nitrous and nitric acids, so these acids when acted upon by reducing agents, might naturally produce ammonia, or in the presence of a decomposing ethyl compound, might give rise to the formation of substituted ammonias. The experiment however seems to prove that while ammonia is a constant result of this reduction, it varies greatly in quantity according to the particular reducing agent employed, and that substituted ammonias are not produced, at least not in recognizable quantities. The following were the reactions observed :—

Reduction by protochlorid of tin.—Alcoholic solution of protochlorid of tin added to nitrite of ethyl causes violent effervescence, but no disengagement of nitrous fumes. The solution of

protochlorid was added until reaction ceased. The whole was then distilled with caustic potash and the resulting gases conducted into dilute chlorhydric acid, which by evaporation left only a film of substance—this gave on examination distinct indications of ammonia.

Reduction by sulphydric acid.—A large quantity of sulphydric acid was conducted through nitrite of ethyl. Slight effervescence was produced and much sulphur deposited. The liquid filtered from the sulphur proved to contain a large quantity of ammonia, but no ethylamine, di-, or tri-ethylamine, although the mode of examination employed would have detected a very small quantity if present. After the removal of the ammonia, the solution heated with Pt Cl_2 gave a small quantity of a brown precipitate of a platinum salt, which when heated glowed for a long time showing the presence of much carbon, and finally left a residue of reduced platinum. The amount obtained was too small for investigation, but 20 or 25 milligrammes of Pt. salt were obtained from the decomposition products of 50 grammes of nitrite of ethyl.

This result therefore, as far as to the production of ammonia, corresponds with that obtained by M. Emile Kopp,* although, as that chemist employed sulphhydrate of ammonia instead of sulphydric acid, it does not appear that the production of ammonia by the reaction itself, could be positively established.

Reduction by ferrous acetate.—Nitrite of ethyl was added to about three times its bulk of ordinary acetic acid, and sufficient alcohol to make them mix. To this mixture iron filings were added. A powerful action set in without aid of heat. Deutoxyd of nitrogen was evolved in considerable quantity. When action had ceased, the resulting liquid was filtered, evaporated with chlorhydric acid and distilled with caustic potash. The distillate contained only traces of ammonia,

The effect of the reducing agents on nitrite of ethyl is therefore very different. Only with sulphydric acid was any considerable quantity of ammonia produced, and only with ferrous acetate was deutoxyd of nitrogen evolved.

3. On the Preparation of Urea from Ferrocyanid of Potassium.

In the preparation of urea by Wöhler's method the amount obtained always falls short of that which should theoretically be produced. Having remarked that even when the operation is

* Gerhardt, *Chimie Org.*, ii, 347.

carefully performed with Liebig's proportions, the lixivate always contains undecomposed cyanid of potassium, it occurred to me to try the effect of a more thorough oxydation, and the result proved very favorable. The following was the course adopted.

Of roasted ferrocyanid of potassium 850 grammes are mixed with 318 grammes of thoroughly dried carbonate of potash in grains, and fused in an iron vessel. When decomposition is complete, the vessel is a little cooled and 1900 grammes of red lead are to be added, not all at once, but 300 to 400 grammes at a time, with intervals of 10 minutes, stirring and keeping up heat enough to retain the whole in a state of fusion.

After the last addition of red lead the mixture is suffered to remain half an hour on the fire to complete the reaction. Heat is applied in all for about four hours. In this way the cyanid of potassium becomes thoroughly oxydized. The process is concluded in the usual manner, and 500 grammes of urea are obtained. No particular precaution is necessary during the fusion, or even the lixiviation with cold water, but in evaporating the solutions the greatest care must be taken to carry off the vapors.

4. *On the Action of Nitric Acid on Picramic Acid.*

On this point very conflicting statements have been made. Girard, and Pugh, respectively state that picric acid is reproduced by the oxydation of picramic acid by nitric acid. A similar statement is made by Kolbe in his *Lehrb. d. Org. Chemie* (authority not given). In a paper published several years since, on picric acid, I expressed a similar opinion. On the other hand Wöhler stated that his nitrohæmatic acid (now known to be identical with picramic) was not reconverted to picric acid by the agency of nitric acid. Gerhardt too, in quoting the first opinion puts a note of interrogation after it, as if to express a contrary conviction. These differences of opinion have induced me recently to re-examine the subject and have led to the conclusion that the substance formed is not identical with picric acid. The following were the reactions observed.

Picramic acid readily dissolves in strong nitric acid to a dark brown solution. By 15 minutes boiling this becomes clear bright red. If then saturated with potash, quantities of nitrate of potash crystallize out, with much brown varnish, but no trace of picrate. After one hour's boiling the color of the solution is considerably lighter—the results much the same.

After four hours boiling the color of the liquid was bright yellow. It was evaporated in the water bath and gave a crystalline substance mixed with much resinous matter. To remove this, it was dissolved in as small a quantity of cold water as pos-

sible, filtered and mixed with half its bulk of strong sulphuric acid. On cooling, a crystalline reddish yellow substance separated which might easily be taken for picric acid mixed with resinous impurity. But neutralized by ammonia and heated with sulphhydrate of ammonia it gave no indications of the presence of picric acid. Tested with cyanid of potassium the results were the same. By spontaneous evaporation of the solution of the substance in ammonia, fan-shaped groups of hair brown needles were obtained. Analysis of these showed conclusively that they consisted of *oxalate of ammonia* disguised by organic matter.

After eight hours boiling the liquid was pale straw yellow and by evaporation on the water bath yielded a substance dissimilar from the former, bright yellow, and colored intensely deep red by cyanid of potassium after previous supersaturation with ammonia. But treated with sulphhydrate of ammonia, it gave no indications of the production of blood red picramate, but became greenish brown with production of a greenish precipitate. The presence of oxalic acid could not be detected.

These experiments appear to me to leave no doubt that picric acid is not formed by the action, either brief, or prolonged, of nitric acid on picramic acid, but that resinous substances are produced, accompanied after a time by oxalic acid, which at a later stage, suffers decomposition itself. All of these substances are however produced in very small amount, the greater part of the constituents of the picric acid passing off in volatile decomposition products.

5. *On the Preparation of Picramic Acid.*

We are generally directed to dissolve picrate of ammonia in alcohol, saturate with ammonia, and then with sulphydric acid. These saturations are tedious and troublesome, and as picrate of ammonia is but sparingly soluble in alcohol much of the latter is consumed, and the solutions are very bulky. The following process will be found greatly preferable.

Picric acid (which is very soluble in strong alcohol) is dissolved in cold alcohol, and excess of sulphhydrate of ammonia added. The liquid then only requires to be evaporated over the water bath, the residue to be exhausted with boiling water, filtered, and treated with acetic acid. The picramic acid obtained in this way is very pure, and the quantity large. In one experiment where the quantities were weighed, over 63 per cent of the weight of the picric acid consumed was obtained. If too little sulphhydrate be used, picric acid remains in the mother water from which the picramic acid crystallizes, and may be recovered by precipitating with carbonate of potash.

Philadelphia, July 13, 1861.

CONTRIBUTIONS TO THE HISTORY OF PICRIC ACID.

BY M. CAREY LEA.

Solubility in Sulphuric Acid.

It is stated in the text-books that picric acid is insoluble in sulphuric acid. It is however soluble to a small degree in strong sulphuric acid; in a more dilute acid it is apparently wholly insoluble, until the dilution reaches a certain point when it increases again. If picric acid be left in contact with oil of vitriol, and the latter be decanted, and mixed with two or three times its volume of water, the picric acid is deposited on cooling in what appear to be very minute square or nearly square scales.

Picric acid crystallizes in the rhombic system, and if we suppose these scales to be formed by predominating $\alpha \bar{P} \infty$ planes bounded at the edges by octahedral planes, they should be rhombs approaching very nearly to squares, having their axes as .9374:1.0000.

If cold saturated aqueous solution of picric acid be mixed with sulphuric acid diluted with an equal volume of water, the following results are obtained:

1 vol. solution of picrate, 4 vols. dilute sulphuric acid. (1 vol. acid, 2 vols. water.)	}	No precipitate, solution remaining as colorless as water.
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1 vol. sol. picric acid, 2 dilute sulphuric acid, same dilution.	}	No precipitate, solution very nearly colorless, faintest tinge of yellow only visible.
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2 vols. solution picric acid, 1 vol. sulphuric acid, same dilution.	}	Nearly the whole of the picric acid was precipitated.
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The amount remaining in solution continued in further trials to diminish as the sulphuric acid became more dilute, until a maximum was reached with

3 vols. solution picric acid, 1 vol. dilute sulphuric acid, same dilution.	}
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It thus appears that mixtures of sulphuric acid and water reach their minimum of solvent power for picric acid when the mix-

ture consists of about 1 vol. acid to 11 vols. water. The proportion of water may be still further increased without materially increasing the solvent power for picric acid. If a cold saturated solution of picric acid be mixed with even but $\frac{1}{17}$ of its volume of sulphuric acid, almost the whole is thrown down.

The fact that the characteristic color of picric acid, which it maintains so persistently through all its combinations, and which is so powerful that, as I have found by actual experiment, a milligramm will distinctly tinge a kilogramm of water, or in other words, that water is colored by one millionth of its weight of picric acid—the fact that this color is totally destroyed by sulphuric acid of a certain strength, without in any way decomposing the acid, is very remarkable. Four volumes of sulphuric acid diluted with five volumes of water exhibit this property, and picric acid dissolves in such a mixture to a colorless solution. This peculiar property has no doubt led to the supposition of the insolubility of picric acid in sulphuric acid above referred to.

Water containing $\frac{1}{100000}$ of picric acid exhibits a bright yellow color. With $\frac{1}{300000}$ the color is still distinct, even in a stratum of not over an inch in thickness. But in large quantities a millionth gives a distinct color as above mentioned.

Tests for Picric Acid.

The best tests for picric acid are

Ammoniacal solution of sulphate of copper, which gives a greenish crystalline precipitate.

Alkaline sulphid with excess of alkali, which with heat gives a deep red liquid.

Alkaline cyanid with ammonia, which when heated gives also a red liquid.

The following table will exhibit the relative sensibility of these reagents:

Strength of aqueous solution of picric acid.	Ammonio sulphate of copper.	Potash liver of sulphur (heat)	Cyanid of potassium.
$\frac{1}{10000}$	Immediate precipitate.	Solution becomes sherry wine red.	Pale sherry red, with heat becoming deep red.
$\frac{1}{40000}$	No precipitate at first, but by standing a few minutes a distinct one.	Deep yellow with a tinge of sherry color.	Deep yellow, tinge of sherry color, deepened by heating.
$\frac{1}{50000}$	Distinct precip. by standing.		
$\frac{1}{100000}$	No precipitate.	The yellow color was slightly deepened, the cyanid test is the more delicate of the two.	

Purification of Picric Acid.

Since my former observations on the purification of picric acid,* I have had occasion to prepare considerable quantities of the acid for my examinations and find that all purifications by converting into potash salt are inapplicable except for very small quantities. The picrate of potash crystallizes out by so small a fall of temperature that the filters, even when kept heated by a double funnel become immediately clogged, and the operation becomes to the last degree tedious and troublesome. As the picrate of lime is very soluble, it seemed probable that it might afford a convenient means of solution; it has indeed been already recommended for that purpose.† But I find it wholly inadmissible. A basic salt is formed which falls to the bottom with the excess of hydrate of lime, and great waste ensues. The insolubility of alkaline picrates in cold alkaline solutions which I have described in a previous number of this Journal, furnished me with an excellent process. The crude acid is saturated with carbonate of soda, an excess of which is to be avoided as it tends to dissolve resinous matter. The hot solution is then easily filtered, and into the filtrate a few clear crystals of carbonate of soda are placed. On cooling, the picrate of soda crystallizes out almost as completely as the potash salt would have done, and all the wearisome delay in filtration is avoided. From the mother water more picric acid may be recovered by the addition of a little carbonate of potash. In decomposing alkaline picrates to separate the acid sulphuric, (and not as usually recommended, chlorhydric) acid should be used, because a moderate excess of sulphuric acid throws down a great portion of the acid which would otherwise remain in the mother water. A moderate but decided excess of acid is absolutely necessary, because otherwise a portion of alkaline picrate escapes decomposition. Even then, it is advisable to recrystallize the acid from alcohol. If picric acid be dissolved by the aid of heat in a solution of sulphate, nitrate, or almost any salt of potash, more or less picrate of potash will crystallize out on cooling. I have thought this process not devoid of interest, because picric must become more extensively known in the laboratory and in the arts than hitherto.

Effect of Reducing Agents.

The effects of reducing agents when alkali is not present, or not present in excess, (in presence of excess of alkali, picramic acid is formed), are very variable, depending upon slight differences which it is very difficult to seize. I subjoin some of the best marked results obtained.

* This Journal, Nov., 1858.

† See Gmelin, Eng. Ed., vol. xi, p. 214.

A mixture of picric acid, alcohol, iron filings, and acetic acid, were digested for an hour at a heat a little below 212° . The filtrate was intensely blue, by standing for half an hour or less, became brown and muddy, depositing a blackish powder, in small quantity, and without trace of crystallization. This filtrate was not changed in color by acids, or apparently affected by them. Alkalies decolorized it. Its shade of blue varied considerably in different experiments, sometimes full blue, sometimes violet, sometimes greenish.

Other experiments were made by acting on picric acid by zinc and dilute sulphuric acid. After an action of some hours, the solution was mixed with alcohol and filtered. The filtrate heated with bicarbonate of potash in successive portions, gave a fine violet liquid, which with further addition of alkali became deep blue with a tinge of violet. According as acid or alkali were present in excess there was more of the violet or blue shade. The colors were always very fugitive, and changed to dirty brown by standing, with deposit of an amorphous blackish powder, (very small in quantity compared with the picric acid used,) which was soluble in acids, and insoluble in alkalies.

These experiments although many times repeated did not lead to the isolation of any substance of interest. There is a certain amount of resemblance between these reactions, and those of some of the decomposition products of phenylamine: the latter contains the radical $C_{12}H_5$, which exists in a substituted form in picric acid.

Philadelphia, April, 1861.

ON THE PRODUCTION OF NEW COLORING MATTERS
BY DECOMPOSITION OF
NITRONAPHTHALINE AND DINITRONAPHTHALINE.
BY M. CAREY LEA.

(1.)

In the process for preparing naphthylamine by the action of acetic acid and iron on nitronaphthaline, the nitronaphthaline is placed in a retort with iron filings and acetic acid, and after the first action has passed off, the contents are heated, a receiver attached and hot lye is added to disengage the naphthylamine. But if a well cooled receiver be attached at the outset of the operation and if heat be applied for some time before the addition of the caustic alkali, a liquid passes over which exhibits the following reactions.

It has a pale reddish color and exhales the disgusting odor of naphthylamine. The pale reddish color becomes pale violet by addition of mineral acids. If it is placed in an open capsule and heated on the sand bath with addition of dilute sulphuric acid, the pale violet color gradually deepens in intensity to rich blue purple. After a time, a black crystalline precipitate falls which must be separated. The brown filtrate by further heating, again becomes rich purple and deposits a further quantity of precipitate. But eventually the liquid becomes muddy brown (A) and yields no more of the precipitate.

This latter is produced at best in extremely small quantity, and sometimes scarcely appears at all—a grain or two is all that can be obtained from 50 or more grammes of nitronaphthaline.

The properties of this very interesting and beautiful substance, as far as could be determined from the very scanty amount obtained for examination* were as follows. As caught on the filter, it constituted nearly black needles with a most brilliant golden green glitter. After being dissolved in alcohol, it was obtained as

* Much to the author's regret he was obliged to discontinue this examination in consequence of an unexplained injurious effect upon his health by manipulating with naphthylamine.

a dark red powder, which when placed on glass and a platinum spatula drawn a few times over it, gave a bright green, almost metallic reflecting surface, contrasting strongly with the red powder around it.

It dissolved somewhat readily in alcohol coloring it an intensely deep blood red. The addition of a very small quantity of sulphuric or nitric acid brought this through a succession of shades as the quantity of acid increased, first ruby, then crimson, then rich purple and finally blue purple, all of the richest shades, and so intense as to require great dilution to render the solution at all transparent. The substance exhibits considerable resistance to acids. The alcoholic solution acidulated with sulphuric acid may be boiled without destroying the color; if nitric acid be substituted, the solution by boiling becomes pale straw color, possibly an effect of the reaction of the nitric acid on the alcohol present.

The production of a red color by alkalies and a blue by acids is becoming characteristic of a large number of organic coloring matters. Amongst these are, the coloring matter obtained by Church and Perkins from tincture of madder; by the resinous body obtained by Schiff in the spontaneous decomposition of naphthylurea; by the body obtained by Church and Perkins from nitrosonaphthaline;* by carotin, as observed by Dr. Husemann;† by a blue coloring matter obtained from picric acid described by myself. The frequency of this reaction is constantly increasing as we become better acquainted with organic coloring matters.

The substance which I have here described would doubtless be valuable as a dye if it could be obtained in sufficient quantity, for the richness of its colors leaves nothing to be desired, but it is only a secondary product in the reaction which produces it. Until it can be obtained in sufficient quantity to admit of its constitution being determined, I propose to call it Ionnaphthine, from *ion*, a violet.‡

(2.)

If the muddy brown liquid mentioned at (A) in the 2d paragraph be treated with liquid ammonia, brown flakes separate. If these be treated with dilute sulphuric acid and bichromate of potash they become black. They then do not dissolve in water or alcohol, but dissolve in dilute nitric acid to a deep violet solution, greatly inferior however in color to the solution of ionnaphthine. This substance may possibly be identical with

* Jahresbericht, 1857, p. 350.

† Chem. Centralb., May 1861, p. 347.

‡ The specimen of this new coloring matter which Mr. Lea has sent to us sustains all he says of its beauty.—Eds.

that described by M. Du Wildes* and obtained by him by oxidizing naphthylamine by means of nitrate of mercury.

(3.)

If the solution of dinitronaphthaline in alcoholic ammonia be heated with solution of sulphite of ammonia, the red solution assumes a rich deep rose color, far richer and more brilliant than the original solution. I have not as yet been able to isolate this substance.

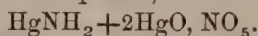
Dinitronaphthaline is as fruitful in colored derivatives as aniline. Treated in solution in alcoholic ammonia with stannous chlorid, it yields a fine blue. Roussin's "artificial alizarine" affords fine shades of purple, the reaction is obtained with great facility. Hofmann and Wood's ninaphthylamine as I have obtained it varies from copper to sealing wax red, but does not seem to me likely to be valuable as a dye. Roussin's alizarine will no doubt be very much so.

NOTE ON A COMPOUND OF AMMONIA, MERCURY AND NITRIC ACID.

BY M. CAREY LEA.

IN the course of an extended examination upon the reactions of the ethyl bases, I noticed that both ethylamine and diethylamine gave with acid solution of mercuric nitrate a white precipitate which is permanent although the solution contains a large excess of acid. This compound did not appear worthy of a special examination as it is no doubt analogous to that formed by ammonia under similar circumstances. But with respect to the constitution of this latter I propose to offer a few remarks.

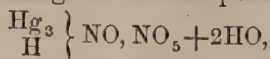
The formula adopted for this compound by L. Gmelin, apparently on the authority of Kane, C. G. Mitscherlich and Pagentecher, whose analyses are quoted, is



This view of the constitution is liable to two objections; first, that it supposes the existence of the bibasic nitrate of mercury

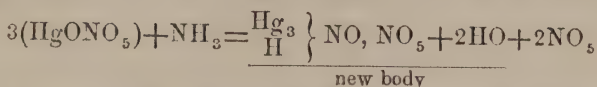
* Rep. de Chimie appliquée, Mai, 1861, p. 172, M. du Wildes is in error in supposing that a reaction which he has obtained is the first instance of a reproduction of an original body from a nitro substitution compound.

in it, which substance is so unstable that it is decomposed by mere contact with cold water; second, that it is unnecessarily complicated. If we assign to the compound the formula



differing from the foregoing by 1 at. H and 1 at. O, we greatly simplify our view of its constitution, and refer it to the class of substituted ammonias.

Adopting this view, we are able to explain its formation by the action of ammonia on mercuric nitrate, by a very natural equation



(unless ammonia be added in excess, the solution always remains strongly acid).

Not only is the formula here proposed more in harmony with the views entertained at the present day, which tend as far as possible to refer such compounds to the ammonia type, but, what is somewhat remarkable, it accords with the analyses of all three of the chemists just mentioned, much better than the formula hitherto adopted. To make this apparent I subjoin them. In the second column opposite the word ammonia I have grouped together the atoms NH_3 derived partly from the substituted ammonia and partly from the 2HO in order to complete the comparison of the results of calculation and analysis.

	Calculated according to the old formula	Calc. by the formula here proposed	Found.		
	$\text{HgNH}_2 + 2\text{HgONO}_5$	$\left. \begin{array}{c} \text{Hg}_3 \\ \text{H} \end{array} \right\} \text{NONO}_5 + 2\text{HO}$	Kane.	C. G. Mitscherlich.	Pagenstecher.
Mercury,	77.72	75.95	76.41	75.47	74.12
Ammonia, $\left\{ \begin{array}{l} \text{Amid} \\ \text{NH}_2 \end{array} \right\}$	4.15	$(\text{NH}_3) 4.30$	3.78	4.40	
Oxygen, (2O)	4.15	$(3\text{O}) 6.08$		6.05	5.92
Nitric acid,	13.98	13.67	12.66	14.33	$\left. \begin{array}{c} \text{NH}_4\text{O} \\ \text{NO}_5 \end{array} \right\} 17.40$
	<u>100.00</u>	<u>100.00</u>		<u>100.25</u>	

It becomes at once evident on inspection that the formula I here propose is greatly more in accordance with the analyses than the old one. The mercury agrees better with all of them; the ammonia and nitric acid at least equally well. But it is (as was to be expected) in the oxygen that the difference is most striking. Mitscherlich and Pagenstecher found 6.05 and 5.92: the new formula gives 6.08, the old 4.15. This would seem to be conclusive.

Philadelphia, Oct. 1st, 1861.

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ON THE PRODUCTION OF THE ETHYL BASES.

BY M. CAREY LEA, PHILADELPHIA.

I MENTIONED in a former number of this Journal that while engaged in the examination of the action of ammonia on certain oxy-ethers, I had met with the experiments of Juncadella and De Clermont, and finding that the production of ethylamine by these reactions had been already indicated, I discontinued my investigations. Subsequently however having occasion to prepare a considerable quantity of ethylamine for other examinations, I determined to ascertain whether the action of nitrate of ethyl on ammonia could not be made use of as a convenient process. Juncadella had already proposed to mix nitrate of ethyl with three or four parts of alcohol, saturate the mixture with dry ammoniacal gas, and heat for two days to 212° in the water bath. This was a rather troublesome process, and a few experiments led me to the following very simple method, which I publish as having given me satisfactory results:

Nitrate of ethyl is mixed with an equal volume of strong alcohol. To this mixture is added a quantity of ordinary strong liquid ammonia equal in bulk to that of the mixture. The nitrate of ethyl is thereby precipitated but is nevertheless easily acted

upon by the ammoniacal liquid. Three hours in the water bath at 212° is generally sufficient to complete the reaction. As the process goes on the nitrate of ethyl becomes brownish, gradually diminishes and finally disappears. The resulting solution does not contain salts of ammonia and ethylamine only, as has been stated, but *a large quantity of diethylamine and triethylamine.*

As the nitrate of ethyl can be prepared in large quantity with great facility by a modification of M. Millon's process, which will appear with some other papers in the following number of this Journal, I am inclined to think that this process will be found valuable for the preparation of the ethyl bases. It is necessary that the tubes should be strong, and not more than two-thirds full. Bottles hermetically sealed are not to be recommended unless extremely strong. In one experiment I operated with four eight ounce bottles all of which stood the test, but on repeating the process three of the four exploded at once and the fourth subsequently.

The presence of alcohol is far from being essential. Nitrate of ethyl is readily decomposed at 212° by aqueous ammonia, and if the ammonia is in considerable excess, the decomposition is complete in three hours. If the excess is only slight the time required for decomposition is greatly increased. In one experiment where 29 parts of nitrate of ethyl were heated with 57 of liquid ammonia, the decomposition was not complete till at the end of 15 hours. The use of alcohol and the proportions above given are what was found to give the most satisfactory result.

Philadelphia, April 9, 1861.

ON THE EXACT SEPARATION OF THE ETHYL BASES.

BY M. CAREY LEA, Philadelphia.

It has been known for some time that when ammonia was acted upon by the halogen ethers, the ethylamine produced was always accompanied by a variable quantity of the secondary and tertiary ethyl bases and the ammonium base, and I have shown that the same is the case with respect to the secondary and tertiary ethyl bases in the reactions of oxy-ethers. The ammonium base I have not looked for, but it is doubtless present also. The primary, secondary and tertiary bases resemble each other so closely in their properties that their separation is attended with great difficulty and has generally been effected by the different solubilities of their chloroplatinates.* I find however that it

* Dr. Hoffman has lately described an elegant mode of separation, differing however, entirely from that here proposed, viz. by means of oxalic ether.

may be accomplished with great ease by means of picric acid. The picrates of the different bases exhibit the most opposite degrees of solubility, the picrate of triethylamine rivalling the picrate of potash in insolubility, while that of diethylamine is soluble to an almost unlimited extent in water, alcohol and ether, without being in the least deliquescent. Its affinity for ether is so great that its concentrated ethereal solution will remain exposed to the atmosphere for days in a syrupy condition, gradually crystallizing on the surface, and eventually all through, to a radiated mass. Between these two extremes the picrate of ethylamine occupies an intermediate position and the differences of solubility are so well marked as to render the separation perfectly easy in the manner to be indicated below.

1. *Separation of the mixed bases from Ammonia.*

This has been generally directed to be done by treating the mixed hydrochlorates either with absolute alcohol, or with a mixture of strong alcohol and ether, whereby the salammoniac is supposed to be left undissolved.

This process I have always found to the last degree unsatisfactory, and necessarily so; for if absolute alcohol be allowed to stand over salammoniac in powder for a time and then be evaporated in a watch glass, a certain quantity of salammoniac will be deposited and the same is true of a mixture of strong alcohol and ether. By operating on the ammonias in the form of sulphates a much more satisfactory result is obtained. For this purpose the mixture as poured out from the pressure tube is treated with a sufficient quantity of pure sulphuric acid to displace the nitric acid (or if bromid or iodid of ethyl have been employed, the bromhydric or iodhydric acid) and the solution is evaporated as far as possible at a temperature of about 250° F. The pasty mass is exhausted with strong alcohol, the alcoholic solution is evaporated as far as possible at the same temperature and the residue exhausted with a small quantity of absolute alcohol. Two exhaustions at least, are necessary even when absolute alcohol is used the first time. In this way a satisfactory result is obtained, which cannot be accomplished with the chlorhydrates.

2. *Separation of the mixed bases from each other.*

TRIETHYLAMINE.

After being completely freed from ammonia as above described, the mixed sulphates were distilled with caustic potash, in the usual way and the bases were saturated with crystallized picric acid. Sufficient heat was applied to redissolve the precipitate which formed toward the close of the saturation, and the hot (not too concentrated) solution allowed to crystallize. The first

crop of crystals thus obtained were purified by several re-crystallizations, the chlorhydrate of the base was formed and from this the chlorplatinate which was obtained in large and beautiful crystals. The platinum salt was analyzed.

·4858 gms. substance gave ·1567 platinum,	Per cent.
This corresponds to	32·26
Chloroplatinate of triethylamine contains	32·23

The close correspondence of the result with the number given by theory indicates the perfect purity of the triethylamine. Its proportion is but inconsiderable compared with that of ethylamine and diethylamine, and it is chiefly contained in the first portion of the gaseous products which pass over in the distillation with caustic potash.

Picrate of triethylamine crystallizes in delicate yellow needles, which dissolve sparingly in cold water and alcohol, abundantly in hot. The decrease of solubility in an aqueous or alcoholic solution as it cools is very sudden, so that a hot solution deposits almost the whole of the salt as it begins to cool. Placed on platinum foil and gently heated, it melts, turns first red, then black, at the same time boiling up, takes fire, and leaves a residue of charcoal.

ETHYLAMINE,

After the least soluble salt had been removed in the manner just described, the mother water deposited another crop of crystals, which were purified by repeated recrystallization, the chlorhydrate of the base was formed, and its chlorplatinate was analyzed.

·4429 gms. substance gave ·1728 platinum.	Per cent.
This corresponds to	39·02
The chloroplatinate of ethylamine contains	39·29

Picrate of ethylamine presents great differences of appearance according to accidental circumstances. When first crystallizing out of the mixed solution it usually forms groups of short brown prisms adhering to the bottom of the basin. If these be recrystallized we obtain long yellow flattened prisms and laminae, extending in every direction through the liquid—few substances exhibit more beautiful crystallization. A dilute alcoholic solution often deposits flat prisms bevelled at the extremities, and sometimes hexagonal plates.

In solubility in water this substance approximates to the picrate of ammonia, to which, after it has been subjected to repeated recrystallizations, it bears considerable resemblance in appearance.

DIETHYLAMINE.

After the picrate of ethylamine has been for the most part removed, the mother waters exhibit a curious phenomenon which

greatly simplifies the further purification of the diethylamine salt left in solution. When these mother waters have been a little reduced by spontaneous evaporation or by a gentle heat, the liquid spontaneously separates into two layers, a pale yellow lighter and a dark brown heavier. The evaporation is continued until the heavier layer constitutes rather more than half of the whole, and then the two layers are separated either at once by a separating funnel, or ether may be added and thoroughly shaken up, when the brown layer dissolves in the ether and rises to the top. After separation it is allowed to crystallize and is once or twice recrystallized from a small quantity of ether by which it is obtained quite pure. A specimen was converted into chlorhydrate and then into chlorplatinate, and gave the following results on analysis:

•3884 gms. substance gave •1377 platinum.	Per cent.
This corresponds to	35.45
chloroplatinate of diethylamine should contain	35.45

It appears therefore that the salt obtained in the above described manner is perfectly pure.

Picrate of Diethylamine without being deliquescent is soluble to almost any extent in water, alcohol and ether. By spontaneous evaporation it crystallizes in a radiated mass. Sometimes at the bottom of the vessel beautiful transparent brown yellow crystals form, which belong to the monoclinic system. Combination observed $\infty P\infty$, $[\infty P\infty]$, $0P$, ∞P , $+P$, and a clinodiamond.

The approximate proportions in which the different ethyl bases were produced by the reaction here made use of were perhaps ten per cent of triethylamine, thirty or forty of diethylamine and fifty or sixty of ethylamine.

The method here described gives with facility a very exact separation of these bases. The only precaution necessary to be observed, especially in operating on small quantities, is that the solution must not be too concentrated at the outset, otherwise the picrate of triethylamine will be mixed with picrate of ethylamine. But the delicate needles of the former are easily distinguished from the broader ones and prismatic crystals of the latter, and two or three recrystallizations suffice to separate them completely.

I feel assured that picric acid will be found to be a most valuable reagent in effecting separations of cognate organic bases. It may be doubted if there exists any other acid whose salts taken as a whole exhibit so marked a tendency to ready crystallization, and the great differences in the solubility of picrates of allied bases, adds, as in the foregoing example, to the value of this acid in effecting separations between them.

Philadelphia, April 9, 1861.

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